National Library
of Canada

Acquisitions and
Bibliographic Services Branch

395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale
du Canada

Direction des acquisitions et
des services bibliographiques

395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file Votre référence

Our file Notre référence

NOTICE

The quality of this microform is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Reproduction in full or in part of this microform is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30, and subsequent amendments.

AVIS

La qualité de cette microforme dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

La reproduction, même partielle, de cette microforme est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30, et ses amendements subséquents.

Canada

UNIVERSITY OF ALBERTA

PYRAZOLYL - METHANE AND -BORATE COMPLEXES OF MOLYBDENUM AND RHENIUM

BY

©

SHAUN DUHAIME

A THESIS SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE.

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

SPRING 1995

National Library
of Canada

Acquisitions and
Bibliographic Services Branch

395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale
du Canada

Direction des acquisitions et
des services bibliographiques

395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file Votre référence

Our file Notre référence

THE AUTHOR HAS GRANTED AN IRREVOCABLE NON-EXCLUSIVE LICENCE ALLOWING THE NATIONAL LIBRARY OF CANADA TO REPRODUCE, LOAN, DISTRIBUTE OR SELL COPIES OF HIS/HER THESIS BY ANY MEANS AND IN ANY FORM OR FORMAT, MAKING THIS THESIS AVAILABLE TO INTERESTED PERSONS.

L'AUTEUR A ACCORDE UNE LICENCE IRREVOCABLE ET NON EXCLUSIVE PERMETTANT A LA BIBLIOTHEQUE NATIONALE DU CANADA DE REPRODUIRE, PRETER, DISTRIBUER OU VENDRE DES COPIES DE SA THESE DE QUELQUE MANIERE ET SOUS QUELQUE FORME QUE CE SOIT POUR METTRE DES EXEMPLAIRES DE CETTE THESE A LA DISPOSITION DES PERSONNE INTERESSEES.

THE AUTHOR RETAINS OWNERSHIP OF THE COPYRIGHT IN HIS/HER THESIS. NEITHER THE THESIS NOR SUBSTANTIAL EXTRACTS FROM IT MAY BE PRINTED OR OTHERWISE REPRODUCED WITHOUT HIS/HER PERMISSION.

L'AUTEUR CONSERVE LA PROPRIETE DU DROIT D'AUTEUR QUI PROTEGE SA THESE. NI LA THESE NI DES EXTRAITS SUBSTANTIELS DE CELLE-CI NE DOIVENT ETRE IMPRIMES OU AUTREMENT REPRODUITS SANS SON AUTORISATION.

ISBN 0-612-01600-5

Canada

Name Shawn Patrick Duhaime

Dissertation Abstracts International is arranged by broad, general subject categories. Please select the one subject which most nearly describes the content of your dissertation. Enter the corresponding four-digit code in the spaces provided.

Chemistry - Inorganic
SUBJECT TERM

0488
SUBJECT CODE

U·M·I

Subject Categories

THE HUMANITIES AND SOCIAL SCIENCES

COMMUNICATIONS AND THE ARTS

Architecture	0729
Art History	0377
Cinema	0900
Dance	0378
Fine Arts	0357
Information Science	0723
Journalism	0391
Library Science	0399
Mass Communications	0708
Music	0413
Speech Communication	0459
Theater	0465

EDUCATION

General	0515
Administration	0514
Adult and Continuing	0516
Agricultural	0517
Art	0273
Bilingual and Multicultural	0282
Business	0688
Community College	0275
Curriculum and Instruction	0727
Early Childhood	0518
Elementary	0524
Finance	0277
Guidance and Counseling	0519
Health	0680
Higher	0745
History of	0520
Home Economics	0278
Industrial	0521
Language and Literature	0279
Mathematics	0280
Music	0522
Philosophy of	0998
Physical	0523
Psychology	0525
Reading	0535
Religious	0527
Sciences	0714
Secondary	0533
Social Sciences	0534
Sociology of	0340
Special	0529
Teacher Training	0530
Technology	0710
Tests and Measurements	0288
Vocational	0747

LANGUAGE, LITERATURE AND LINGUISTICS

Language	
General	0679
Ancient	0289
Linguistics	0290
Modern	0291
Literature	
General	0401
Classical	0294
Comparative	0295
Medieval	0297
Modern	0298
African	0316
American	0591
Asian	0305
Canadian (English)	0352
Canadian (French)	0355
English	0593
Germanic	0311
Latin American	0312
Middle Eastern	0315
Romance	0313
Slavic and East European	0314

PHILOSOPHY, RELIGION AND THEOLOGY

Philosophy	0422
Religion	
General	0318
Biblical Studies	0321
Clergy	0319
History of	0320
Philosophy of	0322
Theology	0469

SOCIAL SCIENCES

American Studies	0323
Anthropology	
Archaeology	0324
Cultural	0326
Physical	0327
Business Administration	
General	0310
Accounting	0272
Banking	0770
Management	0454
Marketing	0338
Canadian Studies	0385
Economics	
General	0501
Agricultural	0503
Commerce-Business	0505
Finance	0508
History	0509
Labor	0510
Theory	0511
Folklore	0358
Geography	0366
Gerontology	0351
History	
General	0578
Ancient	0579
Medieval	0581
Modern	0582
Black	0328
African	0331
Asia, Australia and Oceania	0332
Canadian	0334
European	0335
Latin American	0336
Middle Eastern	0333
United States	0337
History of Science	0585
Law	0398
Political Science	
General	0615
International Law and Relations	0616
Public Administration	0617
Recreation	0814
Social Work	0452
Sociology	
General	0626
Criminology and Penology	0627
Demography	0938
Ethnic and Racial Studies	0631
Individual and Family Studies	0628
Industrial and Labor Relations	0629
Public and Social Welfare	0630
Social Structure and Development	0700
Theory and Methods	0344
Transportation	0709
Urban and Regional Planning	0999
Women's Studies	0453

THE SCIENCES AND ENGINEERING

BIOLOGICAL SCIENCES

Agriculture	
General	0473
Agronomy	0285
Animal Culture and Nutrition	0475
Animal Pathology	0476
Food Science and Technology	0359
Forestry and Wildlife	0478
Plant Culture	0479
Plant Pathology	0480
Plant Physiology	0817
Range Management	0777
Wood Technology	0746
Biology	
General	0306
Anatomy	0287
Biostatistics	0308
Botany	0309
Cell	0379
Ecology	0329
Entomology	0353
Genetics	0369
Limnology	0793
Microbiology	0410
Molecular	0307
Neuroscience	0317
Oceanography	0416
Physiology	0433
Radiation	0821
Veterinary Science	0778
Zoology	0472
Biophysics	
General	0786
Medical	0760

EARTH SCIENCES

Biogeochemistry	0425
Geochemistry	0996
Geodesy	0370
Geology	0372
Geophysics	0373
Hydrology	0388
Mineralogy	0411
Paleobotany	0345
Paleoecology	0426
Paleontology	0418
Paleozoology	0985
Palynology	0427
Physical Geography	0368
Physical Oceanography	0415

HEALTH AND ENVIRONMENTAL SCIENCES

Environmental Sciences	0768
Health Sciences	
General	0566
Audiology	0300
Chemotherapy	0992
Dentistry	0567
Education	0350
Hospital Management	0769
Human Development	0758
Immunology	0982
Medicine and Surgery	0564
Mental Health	0347
Nursing	0569
Nutrition	0570
Obstetrics and Gynecology	0380
Occupational Health and Therapy	0354
Ophthalmology	0381
Pathology	0571
Pharmacology	0419
Pharmacy	0572
Physical Therapy	0382
Public Health	0573
Radiology	0574
Recreation	0575
Speech Pathology	0460
Toxicology	0383
Home Economics	0386

PHYSICAL SCIENCES

Pure Sciences

Chemistry	
General	0485
Agricultural	0749
Analytical	0486
Biochemistry	0487
Inorganic	0488
Nuclear	0738
Organic	0490
Pharmaceutical	0491
Physical	0494
Polymer	0495
Radiation	0754
Mathematics	0405
Physics	
General	0605
Acoustics	0986
Astronomy and Astrophysics	0606
Atmospheric Science	0608
Atomic	0748
Electronics and Electricity	0607
Elementary Particles and High Energy	0798
Fluid and Plasma	0759
Molecular	0609
Nuclear	0610
Optics	0752
Radiation	0756
Solid State	0611
Statistics	0463

Applied Sciences

Applied Mechanics	0346
Computer Science	0984
Engineering	
General	0537
Aerospace	0538
Agricultural	0539
Automotive	0540
Biomedical	0541
Chemical	0542
Civil	0543
Electronics and Electrical	0544
Heat and Thermodynamics	0348
Hydraulic	0545
Industrial	0546
Marine	0547
Materials Science	0794
Mechanical	0548
Metallurgy	0743
Mining	0551
Nuclear	0552
Packaging	0549
Petroleum	0765
Sanitary and Municipal	0554
System Science	0790
Geotechnology	0428
Operations Research	0796
Plastics Technology	0795
Textile Technology	0994

PSYCHOLOGY

General	0621
Behavioral	0384
Clinical	0622
Developmental	0620
Experimental	0623
Industrial	0624
Personality	0625
Physiological	0989
Psychobiology	0349
Psychometrics	0632
Social	0451

UNIVERSITY OF ALBERTA

RELEASE FORM

NAME OF AUTHOR:	SHAUN DUHAIME
TITLE OF THESIS:	PYRAZOLYL - METHANE AND -BORATE COMPLEXES OF MOLYBDENUM AND RHENIUM
DEGREE:	MASTER OF SCIENCE
YEAR THIS DEGREE GRANTED:	1995

Permission is hereby granted to the University of Alberta Library to reproduce single copies of this thesis and to lend or sell such copies for private, scholarly or scientific purposes only.

The author reserves all other publication and other rights in association with the copyright in the thesis, and except as hereinbefore provided neither the thesis nor any substantial portion thereof may be printed or otherwise reproduced in any material form whatever without the author's prior written permission.

Shaun Duhaime

3201, 112 Silvergrove Dr. , NW
Calgary, AB
T3B 5H4

Dated: November 16, 1994

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance a thesis entitled PYRAZOLYL -METHANE AND -BORATE COMPLEXES OF MOLYBDENUM AND RHENIUM submitted by SHAUN DUHAIME in partial fulfillment of the requirements for the degree of Master of Science in Chemistry.

WAG Graham

Professor W. A. G. Graham
Supervisor

Professor J. Takats

Professor J. Campbell

Date: November 16, 1994

ABSTRACT

The synthesis and characterization of pyrazolylalkane rhenium and pyrazolylborate molybdenum and rhenium complexes using 3-trifluoromethyl-5-methylpyrazole (HPf), have been investigated in an effort to define more closely the effect that the 3-CF_3 group exhibits on the size and electronic properties of the tris(3-trifluoromethyl-5-methylpyrazol-1-yl)borate ($HBPf_3$) and bis(3-trifluoromethyl-5-methylpyrazol-1-yl)methane (H_2CPf_2) ligands.

The bispyrazolylalkane H_2CPf_2 was synthesized and reacted with $[Re(CO)_4(\mu\text{-}Br)]_2$ to give *fac*-$H_2CPf_2Re(CO)_3Br$ (**2**). The stereochemistry of **2** was established by an X-ray structure. Reaction of **2** with PMe_3 and PMe_2Ph resulted in the substitution of the pyrazolylalkane ligand by two phosphines affording *fac*-$Re(CO)_3(PR_2R')_2Br$.

Reaction of the tris(3-trifluoromethyl-5-methylpyrazol-1-yl)borate ligand ($HBPf_3$) with $[Re(CO)_4(\mu\text{-}Br)]_2$ resulted in $HBPf_3Re(CO)_3$ (**5**), for which a crystal structure was determined. Photolysis of **5** in tetrahydrofuran substituted one CO, forming $HBPf_3Re(CO)_2THF$ (**6**). The reaction of **6** with PMe_3 resulted in the substitution of the THF, while **6** reacted with Br_2 and CCl_4 to produce the air-stable seventeen-electron radicals $HBPf_3Re(CO)_2X$ (X = Br, Cl), for which magnetic moments were measured.

The complex $[Et_4N]^+$ $[HBPf_3Mo(CO)_3]^-$ (**10**) has been synthesized, and oxidized to the air-stable seventeen-electron radical $HBPf_3Mo(CO)_3^{\cdot}$. The seven-coordinate hydride $HBPf_3Mo(CO)_3H$ was synthesized and its infrared spectrum appeared consistent with a 3:4 coordination geometry (C_s symmetry). However, its NMR spectrum suggested a C_{3v} symmetrical intermediate (3:3:1 coordination geometry) as only a singlet was observed for

the three pyrazole rings, even at -80°C. It is suggested that the molecule is fluxional at this temperature. The reaction of **10** with various nitrosonium salts has revealed a solvent dependency in the yield of $HBPf_3Mo(CO)_2(NO)$ (**13**). Reaction of **13** with bromine, methanol and ethanol afforded stable sixteen-electron molybdenum complexes of the form $HBPf_3Mo(NO)X_2$ (X = Br, OMe, OEt).

ACKNOWLEDGEMENTS

The author expresses sincere appreciation and gratitude to:

Dr. W. A. G. Graham for his encouragement and guidance throughout this work.

The members of Dr. Graham's research group, particularily to Dr. Jim Hoyano and Mr. Dusan Ristic-Petrosic.

Dr. Tom Nakashima and the NMR staff, Mr. Glen Bigam, Mr. Tom Brisbane, Mrs. Gerdy Aarts and Mrs. Lai Kong for high quality NMR spectra.

Mr. John Olekszyk and Mr. Andrew Jodhan for obtaining mass spectra.

Mrs. Darlene Mahlow and Mrs. Andrea Dunn for prompt and accurate microanalytical determinations.

Dr. Josef Takats for enthusiastic discussions.

To other friends made throughout my years at this university, especially Dr. John Washington and Mike Mikoluk.

My family and friends, (especially Christine Frohlich, Maria Garasa and Richard Magner) who will no longer have to endure hearing about it, because now it is in print.

TABLE OF CONTENTS

CHAPTER PAGE

1 INTRODUCTION 1
Section 1 Organometallic Chemistry 2
Section 2 Polypyrazolylborates 3
Section 3 18 Electron Formalism 6
Section 4 Synergic Bonding 10
Section 5 The Nitrosyl Ligand 11
Section 6 Paramagnetic Complexes 15
References 18

2 PYRAZOLYLALKANE RHENIUM COMPLEXES 21
Section 1 Introduction 22
Section 2 Synthesis and Properties of H_2CPf_2........ 24
Section 3 Synthesis and Reactions of $H_2CPf_2Re(CO)_3Br$ 28
Section 4 Experimental 38
References 46

3 SYNTHESIS AND REACTIVITY OF $HBPf_3Re(CO)_3$ 49
Section 1 Introduction 50
Section 2 Synthesis and Properties of $HBPf_3Re(CO)_3$ 52
Section 3 The Reactivity of $HBPf_3Re(CO)_3$ 56
Section 4 The Reactivity of $HBPf_3Re(CO)_2(THF)$ 59
Section 5 Experimental 63

References 75

4 SYNTHESIS AND REACTIVITY OF $HBPf_3Mo(CO)_3^-$ 77

Section 1 Introduction 78

Section 2 Synthesis and Reactions of $[Et_4N]^+ [HBPf_3Mo(CO)_3]^-$ 80

Section 3 The Chemistry of $HBPf_3Mo(CO)_2(NO)$ 90

Section 4 Experimental 95

References 100

5 SUMMARY AND CONCLUSIONS 103

References 107

LIST OF TABLES

TABLE PAGE

CHAPTER 1

1-1 Electrons Donated by Ligands to a Metal Center.................... 10

CHAPTER 2

2-1 $^{13}C\{^1H\}$ NMR Data for H_2CPf_2 26

2-2 ^1H NMR Data for $H_2CPf_2Re(CO)_3Br$ 34

2-3 Drying Reagents for Solvents 38

2-4 Crystal Data and Details of Structure Refinement for $H_2CPf_2Re(CO)_3Br$.. 43

2-5 Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $H_2CPf_2Re(CO)_3Br$.. 44

2-6 Bond Lengths for $H_2CPf_2Re(CO)_3Br$....................................... 45

2-7 Bond Angles for $H_2CPf_2Re(CO)_3Br$... 45

CHAPTER 3

3-1 Comparisons of Crystal Structure Data for $HBPz_3Re(CO)_3$, $HBPz_3{}^*Re(CO)_3$ and $HBPf_3Re(CO)_3$ 54

3-2 Magnetic Moments of Paramagnetic Compounds 8 and 9 63

3-3 Pascal's Constants 69

3-4 Crystal Data and Details of Structure Refinement for $HBPf_3Re(CO)_3$.. 71

3-5 Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $HBPf_3Re(CO)_3$ 72
3-6 Bond Lengths for $HBPf_3Re(CO)_3$ 73
3-7 Bond Angles for $HBPf_3Re(CO)_3$ 74

CHAPTER 4

4-1 ^1H and ^{19}F NMR Data for Pf, $HBPf_3$, and $HBPf_3Mo(CO)_3^-$ 81
4-2 Comparison of Carbonyl Stretching Frequencies for Some 17-Electron Molybdenum Compounds 82
4-3 Stretching Frequencies of Molybdenum Nitrosyl Complexes 93

LIST OF FIGURES

FIGURE PAGE

CHAPTER 1

1-1 Comparison of Cp and $HBPz_3$ Ligands 4

1-2 Numbering of Pyrazole Ring 5

1-3 Molecular Orbital Diagram for an Octahedral Complex 7

1-4 Metal to Carbonyl Bonding Interaction 11

1-5 Molecular Orbital Diagram for Nitric Oxide 12

1-6 Linear and Bent NO Complexes 13

1-7 Resonance Structures for Linear and Bent NO 14

CHAPTER 2

2-1 Boat Conformation of H_2BPz_2M 23

2-2 The H_2CPf_2 Ligand 25

2-3 ^1H NMR of H_2CPf_2 27

2-4 Possible Stereochemical Conformations for $H_2CPf_2Re(CO)_3Br$ 29

2-5 Infrared Spectrum of $H_2CPf_2Re(CO)_3Br$ 30

2-6 Possible Chair Conformation of $H_2CPf_2Re(CO)_3Br$ 31

2-7 ORTEP view of $H_2CPf_2Re(CO)_3Br$ 33

2-8 Inversion of Boat Conformation 35

CHAPTER 3

3-1 ORTEP view of $HBPf_3Re(CO)_3$ 55

3-2 Partial Charges on Carbon Atoms in Pz, Pz* and Pf 58

CHAPTER 4

4-1 Possible Geometries for $HBPf_3Mo(CO)_3H$ 84
4-2 Faller's Proposed Intermediate to Explain Fluxionality 85
4-3 Infrared Spectrum of $HBPf_3Mo(CO)_3H$ 86
4-4 Room Temperature ^1H NMR of $HBPf_3Mo(CO)_3H$ 87
4-5 Methods for Synthesizing $HBPf_3Mo(CO)_2NO$ 89

LIST OF SCHEMES

CHAPTER 3

3-1 Possible Mechanisms for Rhenium Radical Formation 62

CHAPTER 4

4-1 Mechanistic Proposal for the Formation of Dialkoxy Products.. 94

LIST OF ABBREVIATIONS

Me	methyl
Et	ethyl
Ph	phenyl
Cp	η^5-cyclopentadienyl
Cp*	η^5-pentamethylcyclopentadienyl
Pz	pyrazole
Pz*	3,5-dimethylpyrazole
Pf	trifluoromethylmethylpyrazole
$HBPz_3$	trishydrido(pyrazol-1-yl)borate anion
$HBPz^*_3$	tris(3,5-dimethylpyrazol-1-yl)borate anion
$HBPf_3$	tris(3-trifluoromethyl-5-methylpyrazol-1-yl)borate anion
H_2CPf_2	bis(3-trifluoromethyl-5-methylpyrazol-1-yl)methane
allyl	CH_2CHCH_2
THF	tetrahydrofuran
APT	attached proton test
η	descriptor for hapticity
δ	chemical shifts in NMR (ppm)
NMR	nuclear magnetic resonance
IR	infrared
MS	mass spectroscopy
μ	denotes a bridging ligand, or designates micro- (eg. μmol = 10^{-6} mol)
ν	denotes stretching frequency

CHAPTER 1

INTRODUCTION

Section 1

ORGANOMETALLIC CHEMISTRY

In 1827, the synthesis of $K^+[(C_2H_4)PtCl_3]^-$ by Zeise[1] marked the beginning of a new genre of chemical compound which incorporated aspects of both organic and transition metal chemistry. Not surprisingly, these complexes became known as organometallic compounds, representing their unique make-up. Interest in them has developed greatly since that time, in part because of organometallic chemistry's practical applications in organic and industrial use. Their main distinguishing feature is the presence of at least one metal-to-carbon bond, and this provides the generally accepted definition of an organometallic compound.[2]

Zeise's discovery was followed by Schutzenberger's synthesis[3] of $[PtCl_2(CO)_2]$ in 1868, which marked the first metal carbonyl to be made. Then in 1890 Mond,[4] while studying the corrosion of the nickel valves in the reaction vessels, discovered $Ni(CO)_4$. This discovery led to a method for the purification of nickel metal.

It was not until the 1930's that Hieber[5] began his systematic research on metal carbonyl chemistry. Soon after, Sidgwick[6] established the 18 electron formalism, which could be used when considering structural possibilities. Ideas of bonding[7] were not fully developed, and would remain simplistic until the 1950's.

Up to that time, many practical and insightful discoveries had been made. However, organometallic chemistry was not evolving at a rapid rate. Then, in 1951, Kealy and Pauson's discovery of ferrocene[8] sparked new interest into the field. While its true structure was not deduced until the following year, the unique sandwich structure and reactivity attracted immense interest to the field. As well, it aided in the formation of present day bonding theories. Since then, the cyclopentadienyl ligand has been examined extensively to explore its effect on the chemistry of other metal carbonyl and nitrosyl compounds. One of the more interesting compounds is $CpIr(CO)_2$ which was found to activate the C-H bonds in methane.[9]

Organometallic compounds have also proven to be useful in the area of catalysis, and have become a part of such processes as polymerizations, hydrogenations, and hydroformylations. As well, they have become a useful part of organic chemsitry, creating carbon to carbon bonds while maintaining chemoselectivity and synthesizing otherwise inaccessible organic compounds.

Consequently, the area of organometallic chemistry has, and continues to expand into a flourishing division of chemistry.

Section 2

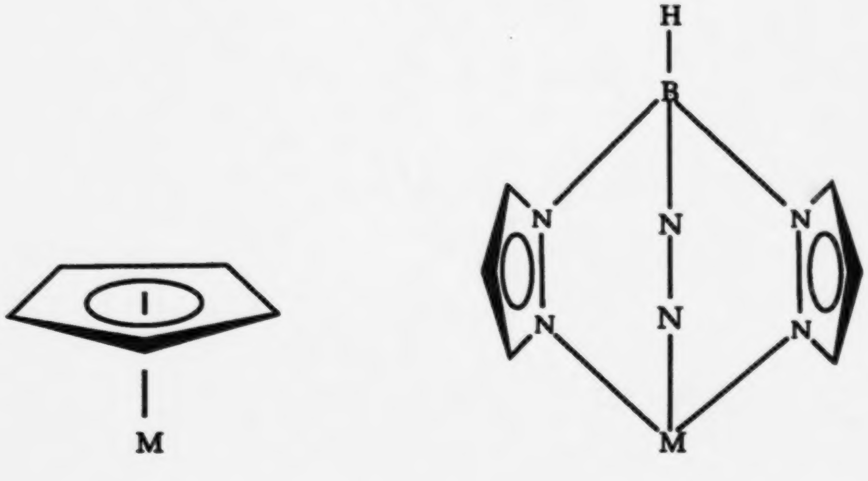
POLYPYRAZOLYLBORATES

Pyrazolylborates were first introduced by Trofimenko[10] in 1967. Since then, extensive investigations into their chemistry on nearly all the transition metals[11] has been accomplished. One attractive feature is their relatively facile synthesis. In principle, heating an excess of pyrazole with KBH_4 until the theoretical number of moles of hydrogen are released (equation (1-1)),

$$KBH_4 + xsPz \xrightarrow{\Delta} KBHPz_3 + 3H_2 \qquad (1\text{-}1)$$

gives the desired ligand. It has also been possible to synthesize bis-and tetrakispyrazolylborates by similar methods.[11a-d]

When trispyrazolylborates were first introduced, comparisons to the Cp and Cp* ligands were made.[12] Both ligands donate six electrons to the metal center, possess a uninegative charge, and occupy (at least formally) three coordination sites on the metal center. This comparison is illustrated in Figure 1-1, where the third pyrazole, going into the page and viewed edge on, is denoted as N-N.



"CpM" "HBPz$_3$M"

Figure 1-1. Comparison of Cp and HBPz$_3$ Ligands

Electronic and steric differences between the two ligands do exist. For example, while many seven coordinate CpMoL$_4$ complexes[13] are known, there have been few reported for trispyrazolylborate analogues.[14] Also, while many dinuclear Cp complexes are formed, few have been identified for the pyrazolylborates.[15] These observations have been attributed to the shielding of the metal from further attack by the larger pyrazolylborate ligand.

Interestingly, the trispyrazolylborate ligand has 10 positions (nine carbon positions and one boron position) which can be altered, while Cp has only five.[11a-d] Consequently, the electron richness and steric requirements of the pyrazolylborate can be easily altered, and this should facilitate new and unique chemistry.

While such immense possibilities exist, the most frequently used pyrazolylborates are the hydrotris(pyrazol-1-yl)borate ($HBPz_3$) and the (3,5-dimethylpyrazol-1-yl)borate ($HBPz^*_3$) ligands, due mainly to their commercial availability. However, exploration of other homo- and heteropyrazolylborates is increasing.[11d]

In 1974, McCurdy used the unsymmetrical MePzH pyrazole[16] to synthesize its corresponding trispyrazolylborate and determined that the reaction was regiospecific. (Figure 1-2 illustrates the numbering scheme of the pyrazole ligand). Trofimenko[17] has also synthesized "second generation" ligands by incorporating large groups, such as t-butyl, mesityl and isopropyl, capable of shielding the metal center of the first row transition metals, in the 3-position of the pyrazole. While it would seem that the unsymmetrical pyrazoles could result in trispyrazolylborates with a mixture of substituents

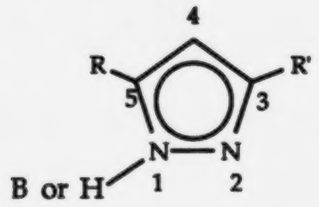


Figure 1-2. Numbering of Pyrazole Ring

in the 3- and 5-positions, this has only been found with one of the second generation ligands.[18] It was believed that the boron would attack the least sterically hindered nitrogen first.[16] However, for the $[HB(Pr^iMeC_3N_2H)_3]^-$ ligand, the isopropyl group (Pr^i) does not exclusively occupy the 3-position. Experimental results indicate that approximately 80% of the ligand formed placed the isopropyl group in the 3-position, the remaining 20% have two pyrazoles with the isopropyl in the 3-position and the third in the 5-position.[18]

Another interesting ligand is (3-trifluoromethyl-5-methylpyrazol-1-yl)borate[19], first prepared in this group by Richard Krentz. It has been shown to promote C-H activation when on rhodium centers, and has provided unique insight into the coordinative stability of alkenes. For example, η^2-ethylene complexes are usually the thermally favored isomer. However, on some of Krentz's complexes this stability is reversed, and on heating, the hydridovinyl isomer is formed.[19a] Consequently, the effect of this ligand on other metal centers is of interest.

Section 3

18 ELECTRON FORMALISM

The 18 electron rule was first proposed by Sidgwick[6] in 1934 and it has proven to be a useful method of predicting a compound's stability and reactivity. The rule refers to the number of electrons which surround the metal center, and can be rationalized by looking at the compound's molecular orbital diagram. (Figure 1-3)

Transition metals contain five nd orbitals (n being the quantum number), three (n + 1)p orbitals, and one (n + 1)s orbital. For octahedral complexes, the six ligand σ orbitals of a_{1g}, e_g and t_{1u} symmetry will interact with the orbitals of the transition metal with similar symmetry, to result in six bonding and six antibonding interactions. The bonding interactions result in a lowering of the energy of both the free ligand and the metal center orbitals, while the antibonding orbitals are higher in energy than both. Figure 1-3 indicates that the t_{2g} set of d orbitals of the transition metal will be nonbonding because there are no ligand orbitals of the appropriate symmetry.

Each of the six ligands can be considered to provide two electrons, thus filling the t_{1u}, a_{1g}, and e_g orbitals. When the metal has a d^6 valence electron count, six more electrons will come from the metal center, and these will fill

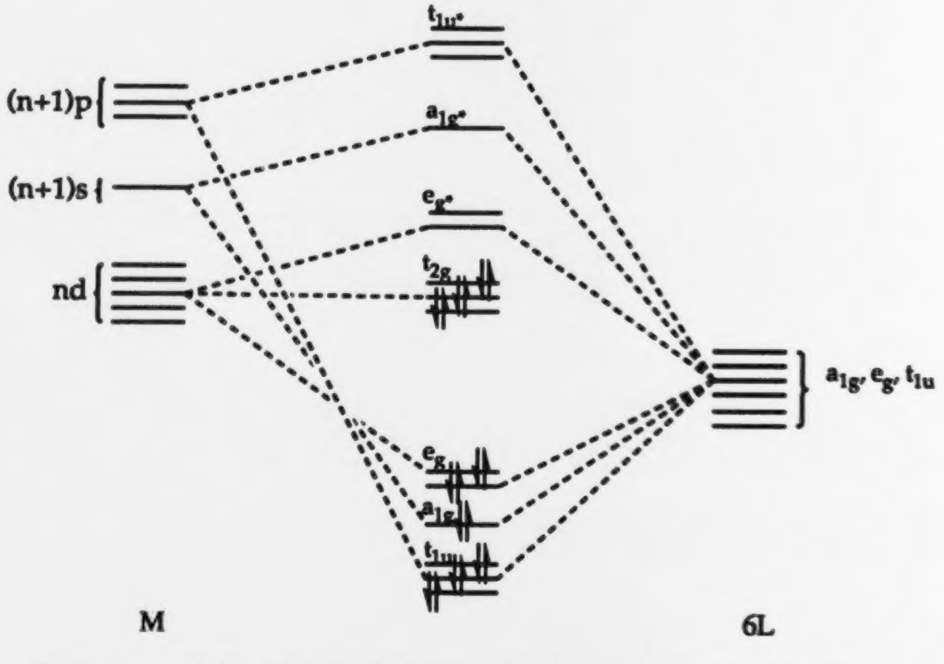


Figure 1-3. Molecular Orbital Diagram for an Octahedral Complex

the t_{2g} nonbonding orbitals. As a result, 18 electrons will be present, but no electrons will occupy the antibonding orbitals, which would destabilize the complex. Stability can be obtained as long as there are no empty, low lying orbitals into which electrons can be easily promoted or which can be subject to nucleophilic attack. Therefore, if less than 18 electrons are present, loss of stability could occur.

Exceptions to the 18 electron rule do exist. Metals surrounded by four ligands (ML_4) having a d^8 electronic configuration can acquire a stable square planar geometry, due to the d orbitals beginning to enter the core, providing less of a contribution to the metal-to-ligand bond. As well, early transition metals do not always conform to the rule. Normally, metal centers will coordinate to either 4 or 6 ligands. However, steric replusions can prevent complexes from attaining 18 electrons. For example, $[Ti(H_2O)_6]^{3+}$ contains only 13 electrons because steric effects prevent additional ligands from approaching the metal center. As well, d and p orbitals of early transition metals can be too high in energy, causing them to play a reduced role in bonding.[2b]

Steric effects can also play an important role in the formation of stable complexes with less than 18 electrons. The 17-electron radical $HBPz^{*}{}_3Mo(CO)_3^{\cdot}$ has been synthesized[20] and found to be quite air stable. Also, Chapter 4 will present 16-electron complexes of the form $HBPf_3Mo(NO)XY$ (where $HBPf_3$ is the tris(3-trifluoromethyl-5-methylpyrazol-1-yl)borate ligand, and X = Y = halogen or alkoxide) which are air stable. One possible explanation[21] for this stability is the size of the pyrazolylborate ligand, and its ability to prevent dimerization and to protect the metal center from further attack.

There are two methods for counting electrons around the metal center. One method assumes the metal to be in the zero oxidation state with the neutral ligands contributing the appropriate number of electrons while ligands such as bromine are considered one electron radicals. For example:

	Ligand	Electrons Donated
$HBPz_3Mo(CO)_3Br$	$HBPz_3^{\cdot}$	5
	Mo	6
	3xCO	6
	$Br^{\cdot}$	1
		18

The pyrazolylborate ligand and the halide are considered to be a radical species, thereby donating only five and one electrons respectively, while the metal center is in the zero oxidation state, possessing six electrons. With each CO donating two electrons, the total count is eighteen.

Alternatively, the second method does not consider bromine or the pyrazolylborate ligand to be a radical, but two and six electron-donating anions, thereby placing the metal center in the two oxidation state.

	Ligand	Electrons Donated
$HBPz_3Mo(CO)_3Br$	$HBPz_3^-$	6
	Mo (II)	4
	3xCO	6
	Br^-	2
		18

Since both methods yield the same result, they are both equally viable, with the choice being based on convenience or custom. Table 1 indicates the number of electrons donated by various ligands.

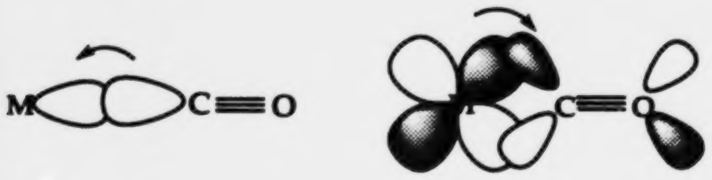
Table 1-1. Electrons Donated by Ligands to a Metal Center

Number of Electrons Donated	Example Ligands
1	Halide and alkyl radicals
2	NO^+, Halide$^-$, R^-, CO, PR_3
3	NO, η^3 - allyl$^\cdot$
4	η^4 - C_4R_4, η^3 - allyl$^-$
5	Cp$^\cdot$
6	Cp$^-$, η^6 - C_6H_6
7	η^7 - $C_7H_7^\cdot$
8	η^8 - C_8H_8

Section 4

SYNERGIC BONDING

The interaction of the metal center and some ligands is described as synergic bonding because bonding results from the donation of electrons from the ligand to the metal, and the back donation of electrons from the metal center to the ligand. However, the degree of sigma donation compared to π acceptor ability for ligands can vary widely. For example, in PR_3 groups the more electronegative the R group, the greater the π acceptor ability of the phosphine ligand. This is a result of the lowering in energy of empty d-orbitals. As well, some ligands (for example, halogens) are π donors. The sigma and π interaction is pictured in Figure 1-4. The σ orbital on the carbonyl will donate a pair of electrons to the metal center (a), while the filled metal d orbital will back donate electrons into the empty π^* orbital of the carbonyl (b). Consequently, the carbon-oxygen bond order will decrease as a larger population of electrons begins to enter the antibonding orbital, while the M-C bond will strengthen.[7]



(a) (b)

Figure 1-4. Metal to Carbonyl Bonding Interaction

A convenient method of determining the extent of M-CO back donation is by observing the position of the CO stretching bands in the infrared. Free CO exhibits an infrared band at 2143 cm^{-1}. However, as the C-O bond order decreases, due to increasing electron density in the π^* orbital, the frequency of the CO bands also decrease. In general, terminal CO stretching frequencies are found in the 2140 - 1800 cm^{-1} region, while bridging CO groups have frequencies in the 1850 - 1700 cm^{-1} region.[22]

Section 5

THE NITROSYL LIGAND

Nitric oxide, like CO, is a π acid ligand capable of forming bonds to transition metals. However, its chemistry is distinct from that of the carbonyl. For example, unlike the carbonyl ligand, NO can bind through either end. Although no isonitrosyl linkages (M-ON) have yet been conclusively determined, complexes have been characterized which contain an η^2-M-N-O-M' structure.[23] The molecular orbital diagram of NO aids in understanding its unique character (Figure 1-5).[24]

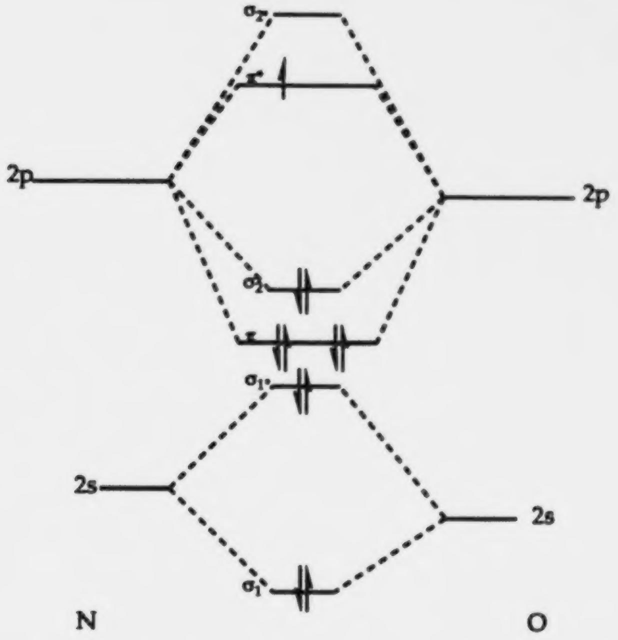


Figure 1-5. Molecular Orbital Diagram for Nitric Oxide

The NO molecule contains 15 electrons: seven from the nitrogen, and eight from the oxygen. Four of these will occupy the sigma bonding and antibonding orbitals from the interaction of the 1s orbitals. The remaining 11 electrons will be placed in the 2s and 2p orbitals. As a result, one electron must occupy the π^* orbital. This is in contrast to the carbonyl ligand, which contains only 14 electrons. Since CO's molecular orbital diagram is similar to nitric oxide's, its HOMO (highest occupied molecular orbital) would be the σ_2 orbital, rather than the π^* orbital for NO. Therefore, the one electron in the π^* orbital appears to play a major role in NO's unusual behaviour.

Bonding of NO to a metal center occurs through the same synergic bonding model used to describe the bonding in CO. There will be donation to the metal through the sigma orbital, and the filled d orbital on the metal will backdonate to the π^* of the NO. However, due to the extra electron in the π^* orbital, an unusual feature also occurs. While terminal CO's are always found to be two electron donors, terminal NO's have been documented to donate either one or three electrons to the metal center, depending on their geometry.[25] Figure 1-6 provides an example of complexes with linear and bent NO bonds. If NO forms a linear bond with the metal (Figure 1-6(a))[26], there will be a net three electron donation, whereas if NO acquires a bent conformation (Figure 1-6(b))[27], only one electron is donated. The linear NO interaction is explained by assuming it to be isoelectronic (containing the same number of electrons) with CO by considering it to be the NO^+ species. Therefore, once NO approaches the metal center, it donates an electron (forming NO^+) and a lone pair thereby donating three electrons. However, in the bent conformation, the metal will donate an electron to the NO, forming NO^-, and then the NO will donate the lone pair. As a result, the net donation is only one electron.

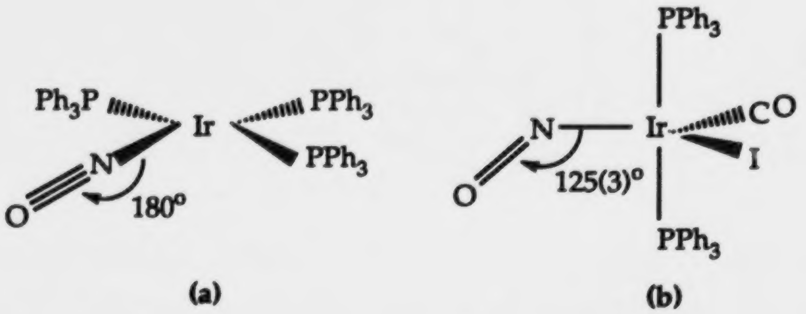


Figure 1-6. Linear and Bent NO Complexes

Infrared spectroscopy is a useful tool in determining bond order changes, and for CO, it can be useful in establishing if terminal or bridging CO's are present. For nitrosyls, which conform to similar bonding modes as carbonyls, more electron donation from the metal center into the π^* orbital results in a weakening of the N-O bond, resulting in a decrease in its infrared stretching frequency. However, it is not possible to conclusively determine the presence of a linear, bridging or bent nitrosyl from the infrared spectrum. This is a consequence of a wide overlapping infrared region for linear, bent and bridging nitrosyls due to N-O bond orders of both one and two being able to exist. This is illustrated by the valence bond resonance structures in Figure 1-7.[24]

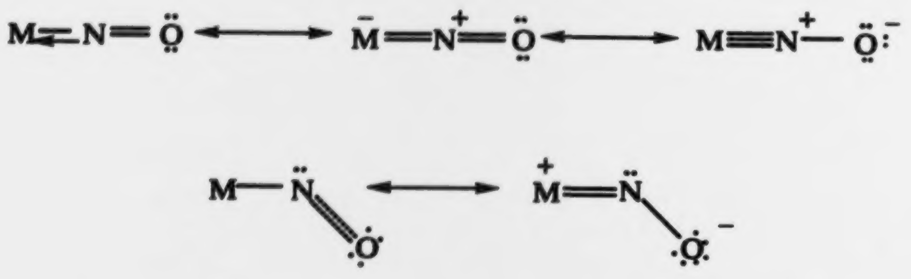


Figure 1-7. Resonance Structures for Linear and Bent NO

Despite the strong similarity with CO, it is important to keep in mind that since N is more electronegative than C, NO will be a better π acceptor ligand than CO. This means that the M-N bond will be strong and the N-O bond will be relatively weak. This is in contrast to CO, where the M-C bond is usually weak, but the C-O bond is quite strong. The importance of this feature lies in predicting the chemistry of complexes containing both NO and CO. Since NO is a better π acid, it will provide added stability to the complex, by widening the HOMO-LUMO gap. Consequently, metal nitrosyl chemistry is quite distinct from that of the metal carbonyl.

Section 6

PARAMAGNETIC COMPLEXES

Complexes containing one or more unpaired electrons are said to be paramagnetic. Even in the absence of a magnetic field, these compounds have a permanent magnetic moment due to their net spin and orbital angular momenta.[28] Although some paramagnetic complexes are easy to predict - such as radicals - others can contain even numbers of electrons and still be paramagnetic. For example, $HBPz^*{}_3Re(CO)(Cl)_2$ contains 16 electrons, yet it is paramagnetic.[29]

Measurement of Magnetic Susceptibility

While conventional NMR data is difficult to obtain for paramagnetic species, other useful information, such as the number of unpaired electrons per unit weight or mole, can be determined by employing NMR techniques.[30] Many methods for determining magnetic susceptibility are available.[31] Only the Evans method[32], which conveniently uses NMR instrumentation and is practical for small quantities of solutions, will be employed in this thesis.

Commercial apparatus designed for use of the Evans method was available in the form of a Wilmad Special Stem Coaxial Insert (196 mm long tube - the top 154 mm has an OD (outer diameter) = 4 mm while the stem has an OD = 2 mm) which was inserted into a standard 178 mm (OD = 5 mm) NMR tube. The inner tube contains a known quantity of compound and internal standard, dissolved in an appropriate deuterated solvent, while the outer tube contains the same internal standard, at the same concentration as the inner tube, dissolved in the same solvent. Two separate lines, both referring to the internal standard, will be observed in the NMR. The line at higher frequency results from the paramagnetic solution.[31b]

The mass susceptibility, χ_g, is determined using equation (1-2), where Δv is the difference between the two lines, in Hz, v is the probe frequency, m is the mass of substance per mL of solution, χ_o is the mass susceptibility of the solvent, d_o is the density of the solvent, and d_s is the density of the solution. The molar susceptibility, χ (cm^3 mol^{-1}), is determined

$$\chi_g = \frac{3\Delta v}{2\pi v m} + \chi_o + \frac{\chi_o(d_o - d_s)}{m} \qquad (1\text{-}2)$$

by multiplying χ_g by the complex's molecular weight. This value is composed of paramagnetic and diamagnetic contributions (1-3). The χ_{dia} value is determined using Pascal's constants (Table 3-2). Therefore, χ_{para} can be determined.

$$\chi = \chi_{para} + \chi_{dia} \qquad (1\text{-}3)$$

For transition metal complexes, the effective magnetic moment, μ_{eff} is usually used, equation (1-4), where χ is the paramagnetic contribution (χ_{para}).

$$\mu_{eff} = 2.828(\chi T)^{0.5} \quad \text{(Bohr Magneton, BM)} \qquad (1\text{-}4)$$

This formula incorporates Curie's law, which stipulates that the magnetic susceptibility must vary inversely with the absolute temperature, yielding a constant value. [30]

REFERENCES

1. Zeise *Pogg. Ann.*, **1827**, *9* , 632.

2. (a). Pauson, P., *Organometallic Chemistry*, Edward Arnold Ltd: London, 1967.

   (b). Lukehart, C., *Fundamental Transition Metal Organometallic Chemistry*, Brooks/Cole Publishing Co.: Monterey, California, 1985.

   (c). Cotton, F. A., Wilkinson, G., Gaus, P., *Basic Inorganic Chemistry*, 2nd Edition, John Wiley and Sons: Toronto, 1987.

3. (a). Schutzenberger, P. *Compt. Rend.*, **1870**, *70* , 1134.

   (b). Schutzenberger, P. *J. Chem. Soc.* **1871**, *24*, 1009.

4. Mond, F. L., Langer, C., Quincke, F., *J. Chem. Soc*, **1890**, *57*, 749.

5. Hieber, *Adv. Organometallic Chem.*. **1970**, *8*, 1-28.

6. Sidgwick, N. V.; R. W., *Proc. Roy. Soc.* **1934**, *144*, 521.

7. (a). Orgel, L. E., *An Introduction to Transition-Metal Chemistry*, Methuen: London, 1962., p 135 - 143.

   (b). Pauling, L., *The Nature of the Chemical Bond*, 3rd Edition, Cornell University Press: Ithaca, NY, 1960, p 331 - 336.

   (c). Richardson. J. W., *Organometallic Chemistry*, (H. Zeiss, ed.), Reinhold: NY, USA, 1960, p 12 - 20.

8. Kealy, T. J.; Pauson, P. L. *Nature* **1951**, *168*, 1039.

9. Hoyano, J.; McMaster, A. D.; Graham., W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190.

10. Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170.

11. (a). Trofimenko, S. *Acc. Chem. Res.* **1971**, *4*, 17.

    (b). Trofimenko, S. *Chem. Rev.* **1972**, *72*, 497.

    (c). Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115.

    (d). Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.

12. O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.

13. Davis, R.; Kane-Maguire, L. P. P., *Comprehensive Organometallic Chemistry*, Pergamon Press: Oxford, England, 1982, vol. 3, p 1177 - 1199.

14. (a). Curtis, M. D.; Shiu, K-B. *Inorg. Chem.* **1985**, *24*, 1213.

    (b). Philip, C. C.; White, P. S.; Templeton, J. L. *Inorg. Chem.* **1992**, *31*, 3285.

    (c). Onyiriuka, E. C.; Storr, A. *Can. J. Chem.* **1987**, *65*, 2464.

    (d). Liu, Y-Y.; Mar, A.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1988**, *66*, 1997.

    (e). Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1988**, *66*, 2194.

15. Shiu, K-B.; Curtis, M. B.; Huffman, J. C. *Organometallics* **1983**, 2, 936.

16. McCurdy, W. H. Jr. *Inorg. Chem*, **1975**, *14* , 2292.

17. Calabrese, J. C.; Trofimenko, S.; Thompson, J. S. *J. Chem. Soc., Chem. Commun.* **1986**, 1122.

18. (a). Rheingold, A.; White, C. B.; Trofimenko, S. *Inorg. Chem.* **1993**, 32, 3471.

    (b). Cano, M.; Heras, J.; Trofimenko, S.; Monge, A.; Gutrerrez, E; Jones, C.; McCleverty, J. *J. Chem. Soc., Dalton Trans.* **1990**, 3577.

19. (a). Ghosh, C. K.; Hoyano, J. K.; Krentz, R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1989**, *111*, 5480.

    (b). Krentz, R., PhD Thesis, University of Alberta, 1989.

20. Shiu, K-B.; Lee, L-Y. *J. Organometallic Chem.* **1988**, *348*, 357.

21. McCleverty, J. A.; Wlodarczyk, A. *Polyhedron* **1988**, 7, 449.

22. Collman, J.; L. Hegedus, L., *Principles and Applications of Organotransition Metal Chemistry*, University Science Books: Mill Valley, USA, 1980.

23. (a). Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Molinari, H.; Sironi, A.; Freni, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1327.

(b). Kyba, E. P.; Kerbi, M. C.; Kashyap, R. P.; Mountzouris, J. P.; Davis, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 905.

24. Richter-Addo, G.; Legzdins, P., *Metal Nitrosyls*, Oxford University Press: NY, USA, 1992.

25. For a sampling of linear and bent nitrosyls, see:

(a). Legzdins, P.; Rettig, S. J.; Sanchez, L. *J. Am. Chem. Soc.* **1985**, *107*, 1411.

(b). Wong, W. K.; Tam, W; Strouse, C. E.; Gladysz, J. *J. Chem. Soc., Chem. Commun.* **1979**, 530.

(c). Pratt, C. S.; Coyle, B. A.; Ibers, J. A. *J. Chem. Soc. (A)* **1971**, 2146.

(d). Mingos, D. M. P.; Robinson, W. T.; Ibers, J. A. *Inorg. Chem.* **1971**, 10, 1043.

26. Albano, V. G.; Bellon, P.; Sanooni, M. *J. Chem. Soc. (A)* **1971**, 2420.

27. Hodgson, D. J.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 1282.

28. Drago, R. S., *Physical Methods in Inorganic Chemistry*, Reinhold Publishing Corp.: NY, USA, 1965, p 389.

29. Gan, L. 1990, PhD Thesis, University of Alberta.

30. Cotton, F. A.; Wilkinson, G.; Gaus, P. L., *Basic Inorganic Chemistry*, 2nd Edition, John Wiley and Sons: Toronto, 1987, p. 63-64.

31. (a). Mulay, L. N., *Magnetic Susceptibility*, Interscience Publishers: NY, USA, 1963, p. 1785-1806.

(b). Drago, R. S., *Physical Methods in Chemistry*, W. B. Saunders Co.: Toronto, 1977, p. 430-431.

32. Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

CHAPTER 2

PYRAZOLYLALKANE RHENIUM COMPLEXES

Section 1

INTRODUCTION

The introduction of the pyrazolylborate ligand has resulted in a wealth of new and interesting complexes.[1] Since then, attempts to vary the electronic and steric properties of the pyrazoles, and, consequently, of the borate ligand, have provided many interesting results.

One variant of the pyrazolylborate ligand is the pyrazolylalkane analogue, $R_nC(Px)_{4-n}$ (where R= hydrogen or an organic group, and Px represents any pyrazole). Investigations[2] since their introduction in 1970 have revealed that they closely resemble the pyrazolylborate ligand in coordinative behavior. Trofimenko suggested[2] that it would be possible to predict the reactivity of the pyrazolylborate ligand if the pyrazolylmethane chemistry were known. However, the properties of the analogous pyrazolylalkane ligands have been less extensively investigated, and therefore are of particular interest.

As with the pyrazolylborate ligand, both the bis- and trispyrazolylalkanes can be synthesized. However, depending on the size of the substituents on the pyrazole ring, synthesis of the trisubstituted ligand may not be possible. For example, the tris(3,5-bistrifluoromethylpyrazol-1-yl)borate is apparently unstable due, presumably in part, to the steric hindrance of the CF_3 groups in the 5-position.[3] In view of the low yields obtained in the preparation of tris(3,5-dimethylpyrazol-1yl)methane,[2] no attempt was made to synthesize the tris(3-trifluoromethyl-5-methylpyrazol-1-yl)methane ligand.

In general, pyrazolylalkane chemistry is rather similar to that of its pyrazolylborate analogues, as Trofimenko suggested. There are two main differences: (1) the pyrazolylalkane is neutral, yielding complexes with an overall charge one unit more positive than that of the borate; and (2) if hydrogen is a substituent on the methylene group, then any effect generated through coordination to the metal center may be monitored by ^{1}H NMR. In contrast, the hydrogens on boron in pyrazolylborate ligands produce signals which are too broad to be observed, due to the quadrupolar nature of boron. As a consequence, information regarding possible conformations can be determined more readily for the alkane analogues.

For complexes of the type $R_2B(Px)_2M$ (where M is a metal center), the B-N and M-N distances and angles result in "puckering" of the ring, causing it to prefer a boat conformation (Figure 2-1). This conformation places one R group toward the metal center, providing the opportunity to interact with

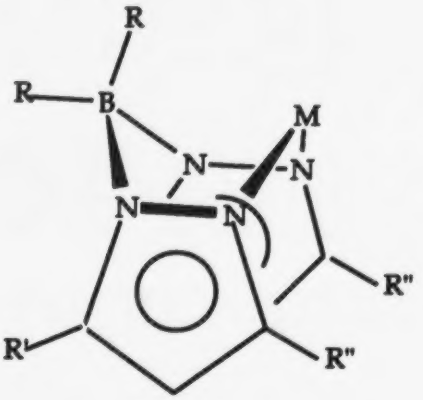


Figure 2-1. Boat Conformation of H_2BPz_2M

electron-deficient metal centers.[4] However, in this Chapter, only eighteen-electron complexes have been synthesized, so an interaction of this kind is not expected.

For these reasons, the synthesis of the bis(3-trifluoro-5-trimethylpyrazolyl)methane ligand, H_2CPf_2 (1), was undertaken. Its reaction with $[Re(CO)_4(\mu\text{-}Br)]_2$ has yielded $H_2CPf_2Re(CO)_3Br$ (2), for which the crystal structure has been determined. Subsequent investigation of the reactions of 2 with PMe_3 and PPh_3 has provided interesting results and information regarding some properties of the ligand.

Section 2

SYNTHESIS AND PROPERTIES OF H_2CPf_2 (1)

The compound 3-trifluoromethyl-5-methylpyrazole (HPf) has been synthesized by various groups,[5] and was first reported in 1964. Synthesis of the bis(3(5)-trifluoromethyl-5(3)-methylpyrazol-1-yl)methane (H_2CPf_2) ligand is illustrated in equation (2-1), and is similar to the method used by Trofimenko[2] in preparing other pyrazolylalkanes. Addition of potassium

$$\begin{aligned} \mathrm{HPf} + \mathrm{K(s)} &\xrightarrow[\mathrm{THF}]{\Delta} \underset{\mathbf{a}}{\mathrm{K^{+}Pf^{-}}} \\ \mathrm{K^{+}Pf^{-}} + \mathrm{CH_2I_2} &\xrightarrow[\text{neutral pH}]{\Delta} \underset{\mathbf{1}}{\mathrm{H_2CPf_2}} \end{aligned} \qquad (2\text{-}1)$$

metal to the 3-trifluoromethy-5-methylpyrazole solution removed the N-bound proton, and produced the pyrazolide nucleophile **a**. Reaction of **a** with diiodomethane was very slow (requiring over 50h), and was continued until a neutral pH was obtained. Following trituration and recrystallization, 1 was obtained as a white solid.

The CF_3 and CH_3 groups in 1 could be positioned in either the 3- or 5-positions since the pyrazolide anion is, in principle, an ambident nucleophile. However, spectroscopic data indicate the formation of only one, symmetrical compound. It has been speculated[6] that the proposed transition state for the synthesis of the pyrazolylborate ligand favors attack at the least favored nitrogen. However, Krentz[3] has shown, by means of X-ray structures, that in the reaction of HPf with KBH_4, only the tris(3-trifluoromethyl-5-methylpyrazoly-1-yl)borate ligand is obtained. This, in conjunction with the successful crystal structure determination of $H_2CPf_2Re(CO)_3Br$, seems to support the assumption that the CF_3 group resides in the 3-position.

The H_2CPf_2 ligand is shown in Figure 2-2, and its ^{13}C data are compiled in Table 2-1. The C-F coupling constants are within the 265 - 290 Hz

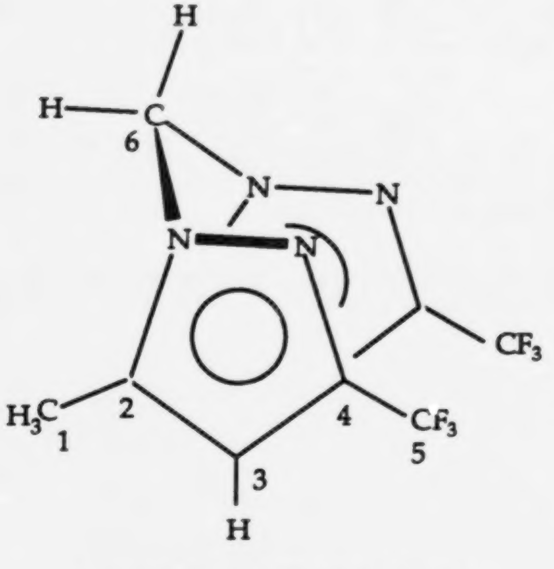


Figure 2-2. The H_2CPf_2 Ligand

range for a CF_3 group attached to an aromatic compound, while the two-bond C-F coupling value is consistent with values found in fluorinated alkanes (22 - 61 Hz).[7]

Table 2-1. $^{13}C\{^1H\}$ NMR Data for H_2CPf_2[a]

Shift (δ)	Multiplicity	Assignment	Coupling (Hz)
11.38	s	C1	-
61.11	s	C6	-
105.79	s	C3	-
122.90	q	C5	270
143.52	q	C4	36
144.46	s	C2	-

a. In CD_3NO_2

At ambient temperatures, the ^1H NMR exhibited three peaks: a doublet at δ 2.53 ppm (J = 0.8 Hz) and two singlets at δ 6.28 and δ 6.32 ppm. Although the doublet can be assigned to the 5-methyl group on the pyrazole ring, further investigation was necessary to unambiguously assign the two singlets to the hydrogens on carbon 3 or 6 (Figure 2-2).

Assignment of these peaks was aided by the coupling observed. Irradiation of the doublet at δ 2.53 ppm should sharpen the peak to which it is coupled. Figure 2-3(a) and (c) show the initial spectrum, while (b) and (d) are the result of irradiation. The peak at δ 6.28 ppm retains its half-height width, while the δ 6.32 ppm peak has narrowed. Consequently, the former may be assigned to the two hydrogens on the methylene unit, and the latter to the 4-H on the pyrazole rings.

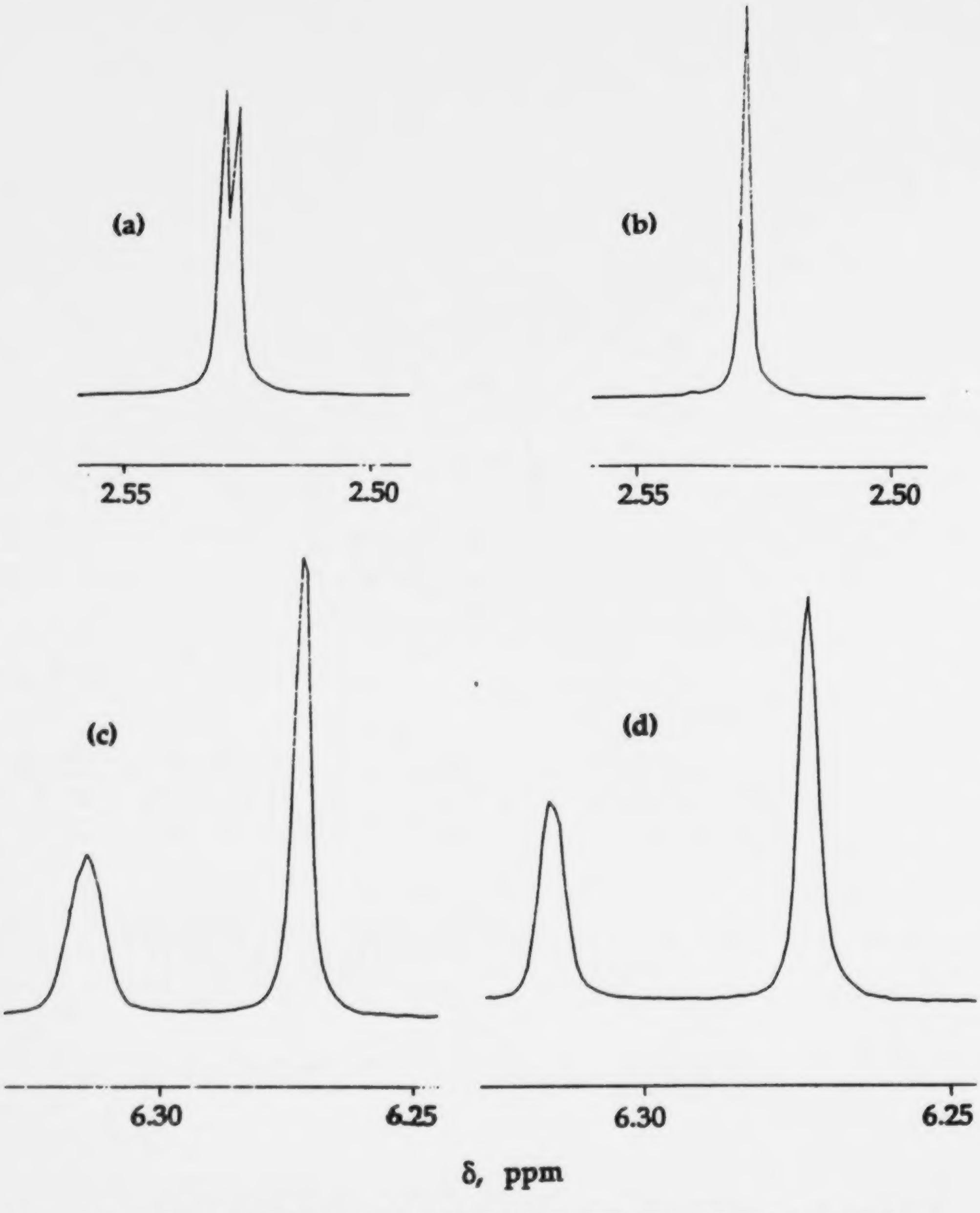


Figure 2-3. ^1H NMR Spectrum of H_2CPf_2 in CD_2Cl_2. Upper traces show methyl region (a) without irradiation and (b) with irradiation at δ 6.32. Lower traces show CH_2 and pyrazole 4-H region (c) without irradiation and (d) with irradiation at δ 2.53. Peak intensities of upper and lower spectra have been arbitrarily adjusted and should not be compared.

Section 3

SYNTHESIS AND REACTIONS OF $H_2CPf_2Re(CO)_3Br$ (2)

Refluxing **1** with $[Re(CO)_4(\mu\text{-}Br)]_2$ in THF resulted in the formation of $H_2CPf_2Re(CO)_3Br$ (**2**) in approximately 55% yield (equation 2-3). This ivory complex could be recrystallized by cooling its dichloromethane solution to -30°C for several days.

$$\underset{\mathbf{1}}{H_2CPf_2} + 1/2\,[Re(CO)_4(\mu\text{-}Br)]_2 \longrightarrow \underset{\mathbf{2}}{H_2CPf_2Re(CO)_3Br} \qquad (2\text{-}3)$$

This reaction creates a six membered ring, containing four nitrogen atoms, the carbon atom of the methylene unit, and rhenium, and permits the formation of two possible geometries: one containing the bromine in the axial position, and one with bromine in an equatorial site ((a) and (b) respectively in Figure 2-4). If the bromine is in the axial position, it could either be closer to the methylene unit or to the pyrazole rings. Since the cone angles[8] for CO and Br are 95° and 105° respectively, it would seem likely that due to steric interactions between bromine and the CF_3 groups, the bromine would prefer a position closer to the methylene unit. If it occupies an equatorial site, two enantiomers would result. For simplicity, only one axial and one equatorial illustration are presented. Below each structure is a simplified representation which identifies each as having *fac* or *mer* stereochemistry at the rhenium center.

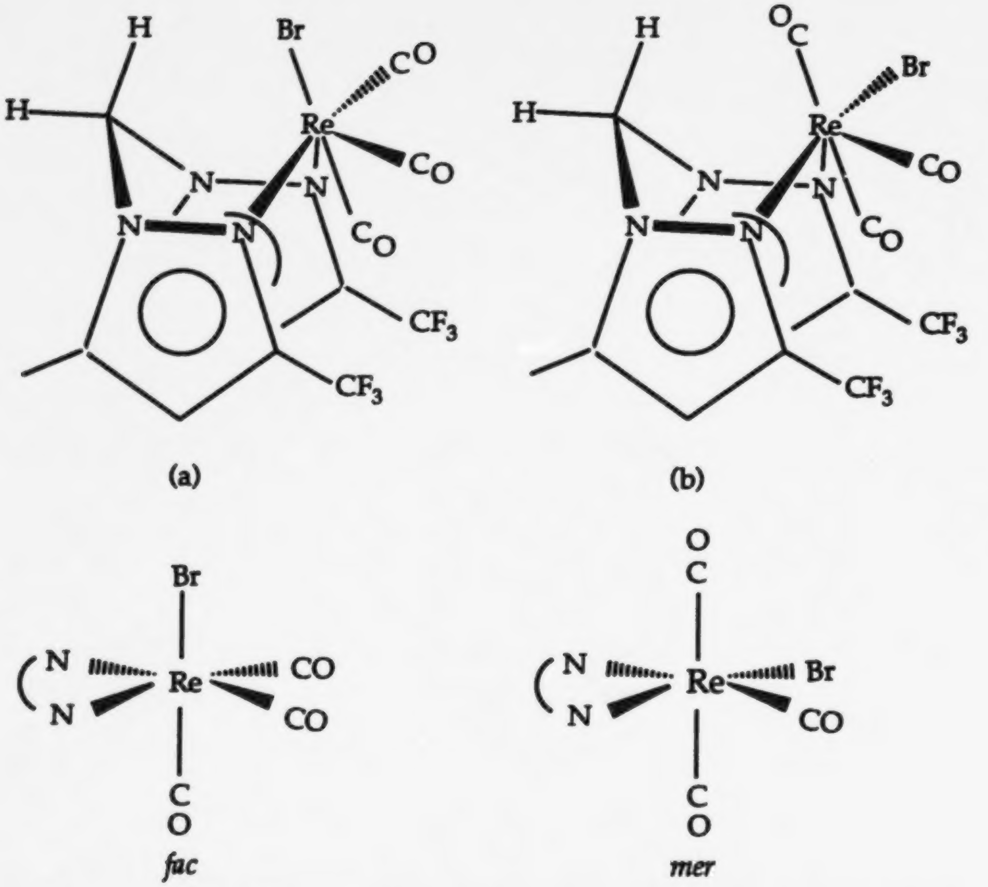

H
Br
CO
H
Re
N
N
CO
N
N
CO
CF3
CF3
(a)
H
OC
Br
H
Re
N
N
CO
N
N
CO
CF3
CF3
(b)
Br
N
N
Re
CO
CO
CO
fac
OC
N
N
Re
Br
CO
CO
mer

Figure 2-4. Possible Stereochemical Conformations for $H_2CPf_2Re(CO)_3Br$

The infrared spectrum of **2** (Figure 2-5) exhibited three carbonyl stretching bands within the 2200 - 1600 cm^{-1} region. Having the bromine in the axial position (a) creates a mirror plane, resulting in C_s symmetry, while (b), containing no plane, has C_1 symmetry. Unfortunately, character tables predict the presence of three bands for the carbonyl ligands for both symmetry groups: (2A' + A") for C_s symmetry and (3A) for C_1 symmetry groups. However, by observing the relative intensities of the infrared bands it is possible to establish with reasonable certainty whether the facial or

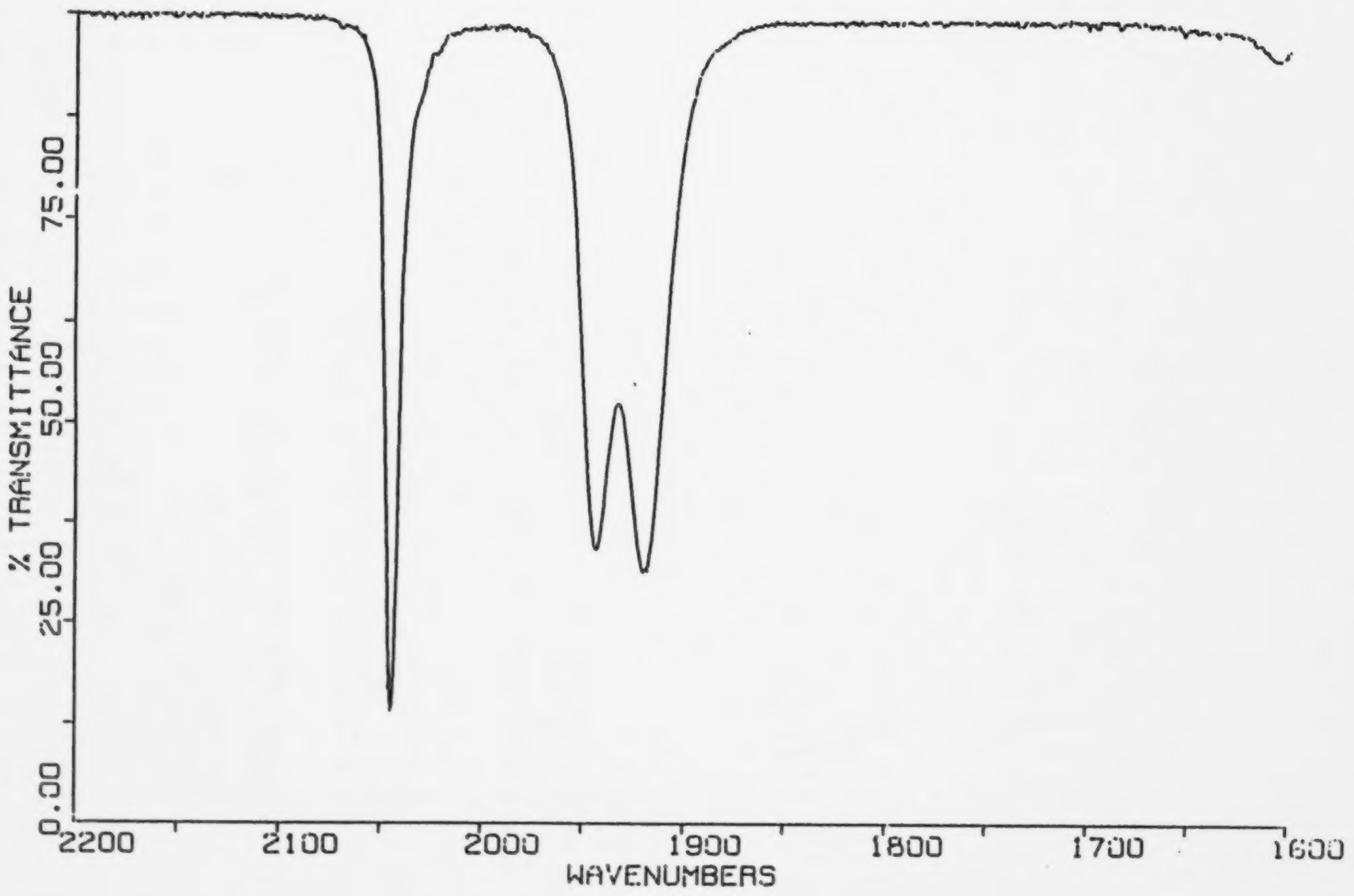


Figure 2-5. Infrared Spectrum of $H_2CPf_2Re(CO)_3Br$ (2) $(CHCl_3)$

meridional isomer is present.[9] In this case, the three bands are of near equal intensity, which is consistent with the infrared spectrum of a *fac* isomer.

The ^{19}F NMR spectrum of **2** consisted of a singlet, while the ^{1}H NMR contained a doublet for the 5-Me protons and the inner two peaks of a quartet for the 4-H protons on the pyrazole rings. The presence of these multiplets is a consequence of the coupling between the 5-Me and the 4-H of the pyrazole ring. These data confirm the presence of a plane of symmetry, and suggests structure (a) to be the most plausible alternative, since (b) would place the pyrazole groups in different environments, which would result in two singlets in the ^{19}F NMR.

Organic six-membered rings usually adopt either a chair or twist conformation.[10] Here, though, the chair conformation is unlikely, as it would require the near planar three coordinate nitrogen to rehybridize to a pyramidal configuration, which would result in the loss of aromaticity in the pyrazole ring (Figure 2-6).

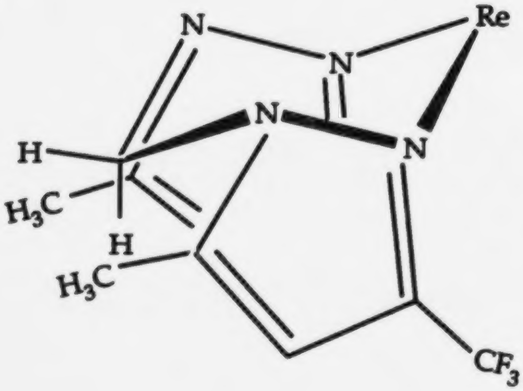


Figure 2-6. Possible Chair Conformation of $H_2CPf_2Re(CO)_3Br$

Carbon-13 NMR data could not be obtained for all the carbon atoms of the complex due to its low solubility. However, signals for the 5-Me (11.52

ppm), CH_2 (58.89 ppm), and 4-CH (110.03 ppm) carbons were observed. Compared to the uncoordinated ligand, the two carbons which are part of the pyrazole show some movement downfield, with the 4-C incurring the largest shift (approximately 5 ppm), possibly as a result of the donation of electrons to the metal center upon coordination. Of the three signals observed, it would be expected that the 4-C of the pyrazole ring would undergo a largest shift since it is part of the pyrazole ring.

X-Ray Structure of $H_2CPf_2Re(CO)_3Br$ (2)

Confirmation of the structure of **2** was provided by an X-ray structure (Figure 2-7) carried out by Dr. R. McDonald of the Structure Determination Laboratory of this Department. It shows a boat conformation, with the bromine in the axial position, pointing toward the methylene group. A crystallographic mirror plane is present running through the hydrogens on the methylene group, the metal center, and the axial bromine and carbonyl. This is consistent with the spectroscopic data obtained. Bond angles indicate that the rhenium has a slightly distorted octahedral conformation, while the carbon of the methylene unit has a slightly distorted tetrahedral environment.

The Re-N bond length is 2.263(5)Å, which is longer than that found in $PhPPz^*_2Re(CO)_3Br$ (2.18(4)Å)[11] and $HBPz^*_3Re(CO)_3$ (2.174Å).[12] The Re-Br bond length (2.6569(10)Å) is within the acceptable range of 2.469-2.769Å, while the M-C-O bond angles for **2** (175.4(9)°, 176.0(7)°) are similar to values for $PhPPz^*_2Re(CO)_3Br$ (174(6)°, 171(5)°, 165(5)°), and $HBPz^*_3Re(CO)_3$ (176.7(2)°, 178.7(2)°).

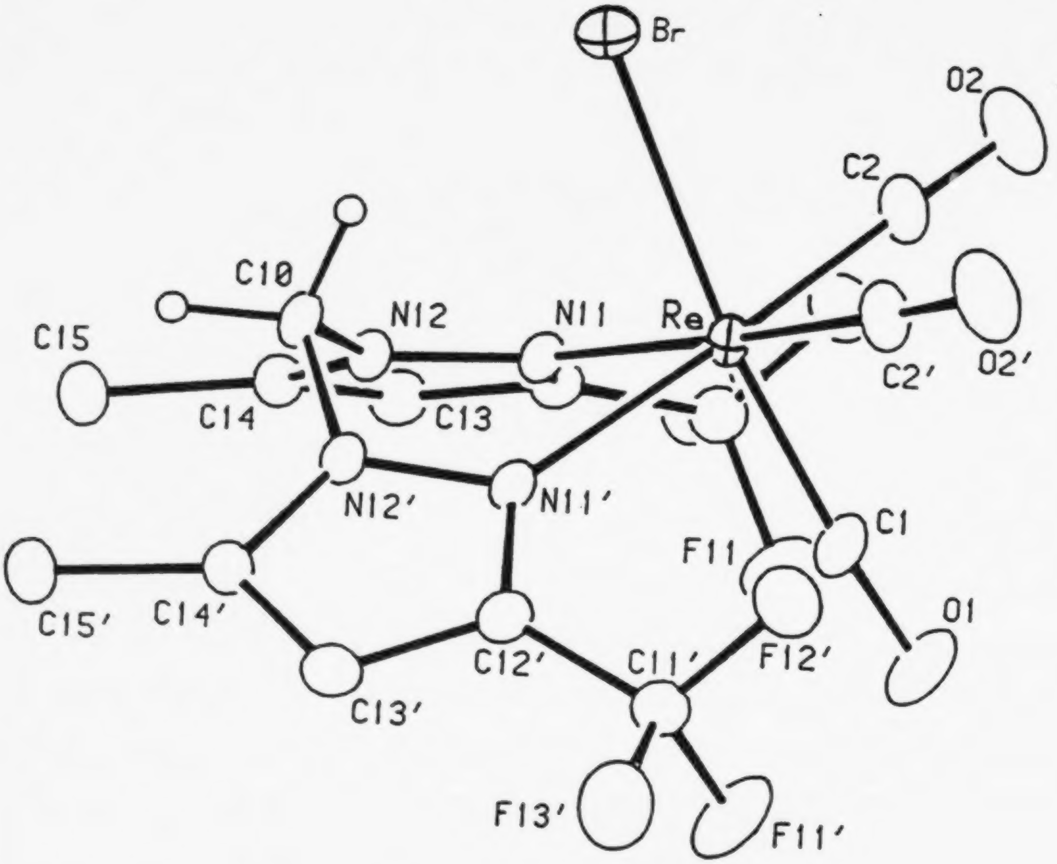

Br
O2
C2
C10
N12
N11
Re
C15
C14
C13
C2'
O2'
N12'
N11'
F11
C1
C15'
C14'
C12'
C11'
F12'
O1
C13'
F13'
F11'

Figure 2-7. ORTEP view of $H_2CPf_2Re(CO)_3Br$ (2)

The axial hydrogen of the methylene group is 3.09Å from the rhenium center, and 2.48Å from the bromide, while the carbon and nitrogen atoms of the pyrazole rings are within 0.01Å of the two planes which incorporate them, and which meet at a 56.1° angle.

Attempted Ring Inversion

Room temperature ^{1}H NMR data for **2** are presented in Table 2-2, and suggest a non-fluxional molecule. Storr has shown[13] that in some bispyrazolylgallate boat complexes a boat inversion occurs (Figure 2-8), and has proposed a pathway which includes a planar intermediate. Activation parameters between 40 - 70 KJ/mol were obtained. However, other pyrazolylgallate complexes, such as $(Me_2GaPz^*{}_2)Rh(CO)(PPh_3)$, do not exhibit fluxional behavior at room temperature due, presumably (as Storr has suggested), to interactions between the substituent groups on the pyrazole ring and the PPh_3 group.[14] It is likely that ring substituents markedly influence the activation barrier.

Table 2-2. ^{1}H NMR Data for $H_2CPf_2Re(CO)_3Br^a$

Shift (ppm)	Assignment	Multiplicity^b	Coupling(Hz)
2.59	5-Me	d	0.4
6.04	CH_2 (eq)	d	15
6.74	4-H	q	0.4
8.78	CH_2 (ax)	d	15

a in CD_2Cl_2, ambient temperatures
b d = doublet, q = quartet

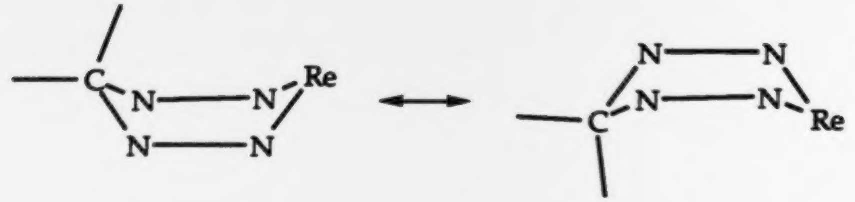


Figure 2-8. Inversion of Boat Conformation

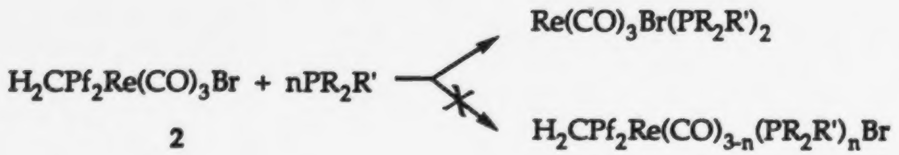
In an attempt to observe ring inversion in 2, its ^1H NMR was monitored as a solution was heated. Up to 40 °C, no change was observed. At 60 °C, new peaks began to appear, indicating the decomposition of the starting material. This was confirmed by running a subsequent room temperature spectrum and noting the continued presence of these signals. Applying Storr's postulate[14] that the activation barrier to reach the planar intermediate is influenced by the interaction of the pyrazole substituents with the ligand, the methyl and trifluoromethyl substituents in 2 could increase the activation barrier, so that the complex decomposed before inversion took place at an observable rate. It should be remembered, however, that in contrast to Storr's systems, inversion of 2 would result in a different and energetically less favorable isomer.

In the ^1H NMR spectrum of the free ligand 1, a singlet at δ 6.28 ppm represented the hydrogens on the methylene group. In the coordinated ligand, though, they are doublets at δ 8.79 and 6.04 ppm with a coupling constant of 15 Hz. Therefore, one proton has shifted only slightly upon coordination, while the other has moved over 2.5 ppm downfield. This coupling value is within the range 12-15 Hz for geminal hydrogen of a locked six membered ring,[15] however, this large downfield shift is unusual. For instance, when $H_2CPz^*_2$ coordinates in $H_2CPz^*_2Mo(CO)_2(\pi\text{-allyl})Br$ the difference between the signals for the CH_2 protons is only 0.3 ppm.[16] Since one methylene hydrogen is bent toward the metal center and the bromide ligand, with distances of 3.09Å and 2.48Å respectively, one might suppose that it is being deshielded by these two groups, and consequently is found farther downfield than expected. It is also possible that there is a weak Br-H interaction, resulting in the deshielding of the proton.

Reactions of $H_2CPf_2Re(CO)_3Br$ (2)

The infrared spectrum of 2 exhibited three CO stretching bands at 2045, 1943 and 1920 cm^{-1}. In view of these relatively high frequency bands, it was assumed that reaction with PMe_3 or PMe_2Ph would result in the substitution of a carbonyl by the phosphine. As the phosphine was slowly added at room temperature, three new bands appeared in the infrared spectrum at lower frequency than the starting material. Although only two bands would be expected for a monosubstituted product, it may be that two carbonyls were substituted, giving a mixture of mono- and disubstituted products, or that isomers have formed. However, examination of the ^{19}F NMR indicated a singlet at -63.52 ppm, which is identical to the value of the free ligand 1. Therefore, reaction with the phosphine resulted in the substitution of the ligand by two phosphine molecules (equation (2-4)). Attempts to rigorously control the stoichiometry in order to observe an η^1-(H_2CPf_2) intermediate, or product, were not successful.

Compounds 3 and 4 have been previously synthesized by Singleton.[17] A comparison of infrared band intensities and values indicated the formation of the *fac* isomer in each instance. A mass spectrum was also obtained as further proof of their identity.



$$H_2CPf_2Re(CO)_3Br + nPR_2R' \longrightarrow Re(CO)_3Br(PR_2R')_2$$

$$H_2CPf_2Re(CO)_3Br + nPR_2R' \not\longrightarrow H_2CPf_2Re(CO)_{3-n}(PR_2R')_nBr \quad (2\text{-}4)$$

2

R = R' = Me 3 n = 1 or 2
R = Me, R' = Ph 4

Loss of the bispyrazolylmethane ligand when other nonchelating ligands are present has been previously observed.[16,18] It has been proposed[18b] that the displacement of the bispyrazolylalkane is a result of favorable energetics. That is, the pyrazolylalkane, once dissociated, is able to adopt a more stable (less strained) configuration requiring less energy. Thermochemical data for complexes of the form $L_2Mo(CO)_4$ have indicated that when L is 1,10-phenanthroline, the complex is 5 kcal/mol more stable than when L is 2, 2'-bipyridine.[19] While the displaced bipyridine can revert to a preferred conformation of lower energy, no such energy gain would be realized for the phenanthroline ligand.

The crystal structure of 2 indicates only a slightly distorted tetrahedral conformation around the methylene group (111.0(6)^{o} vs 109.5^{o}), with the two pyrazole rings pointing away from one another. Consequently, Lobbia's suggestion that the ligand's facile displacement could be due, in part, to its adoption of a less strained (lower energy) conformation, is not likely important in this case. Entropy would not be the driving force for the reaction since three reactant molecules react to form two product molecules. Thus it appears to be a matter of relative ligand-metal bond energies. The X-ray structure of 2 indicated longer Re-N bond lengths, possibly as a result of the CF_3 groups on the pyrazole rings. This suggests a reduced Re-N bond strength, with the result that the Re-CO bonds are stronger and less prone to substitution.

Section 4

EXPERIMENTAL

All manipulations were carried out under an inert atmosphere of prepurified argon, using standard Schlenk techniques. $[Re(CO)_4(\mu\text{-Br})]_2$ was synthesized according to literature methods.[20] Complexes showed oxygen sensitivity in solution, but solids could be handled in air for prolonged periods of time, without decomposition. The HPf ligand was synthesized according to Krentz.[3]

General Techniques

Solvents were dried according to Table 2-3, under argon, and from the appropriate drying reagent. Acetonitrile was distilled over phosphorous pentoxide prior to storage over the calcium hydride. Deuterated solvents were dried by the same method as the regular solvent, and were stored over molecular sieves. All other solvents were either stored over molecular sieves, or used as received from suppliers.

Table 2-3. Drying Reagents for Solvents

Solvent	Drying Reagent
Dichloromethane	Calcium Hydride
Acetonitrile	Calcium Hydride
Hexane	Na-K alloy
Benzene	Potassium metal
Methanol	Drierite
Tetrahydrofuran	Sodium metal/benzophenone
Nitromethane	Calcium Chloride

Glassware was cleaned using a KOH-Ethanol solution, followed by treatment with an HCl solution and was then dried in a 160 °C oven, prior to use.

Infrared spectra were obtained using an Nicolet MX-1 FTIR spectrometer, scanning over the 2200 - 1600 cm^{-1} region, with a 0.5 mm KBr cell. Unless otherwise specified, proton, fluorine, and carbon NMR were collected at ambient temperatures using Bruker WH-200, Bruker AM-300 and Bruker AM-400 spectrometers. Samples were either septa sealed under argon or flame sealed under vacuum.

Elemental analyses were carried out by the Microanalytical Laboratory of this department. Mass spectra were recorded on an A.E.I. MS-12 Spectrometer.

Preparation of $H_2C(3\text{-}CF_3\text{-}5\text{-}MePz)_2$ (1)

Potassium metal (3.15 g, 80.6 mmol) in 150 mL THF was added to HPf (15.00 g, 99.9 mmol) in 100 mL THF and refluxed overnight. After removing the orange solution from heat and cooling, CH_2I_2 (3.12 mL, 11.6 mmol) was added. This solution was refluxed for approximately 52 hours, at which time, the pH was neutral (determined by using pH paper). The THF was removed by the rotary evaporator, and the residue triturated in 10 mL heptane. The solution was filtered, and the precipitate washed with heptane (5 x 5 mL) yielding a white solid (5.31 g, 44%).

Characterization: MS, 120 °C/70 eV (m/e, rel. int.): M^+ (312, 76), M-Pf^+ (162, 100), Pf^+ (150, 3). ^1H NMR (CD_2Cl_2): δ 2.53 (d, 6H, $^4J_{H-H}$ = 0.6 Hz), 6.28 (s, 2H), 6.32 (s, 2H). ^{19}F NMR (CD_2Cl_2): δ -63.53 (s, 6F). ^{13}C APT NMR (CD_3NO_2): δ 11.38 (s, CH_3), 61.11 (s, CH_2), 105.79 (s, CH), 122.90 (q, CF_3, J_{C-F} = 270 Hz), 143.52 (q, C-CF_3, $^2J_{C-F}$ = 36 Hz), 144.46 (s, C-CH_3). Anal. Calcd for $C_{11}H_{10}N_4F_6$: C 42.32 , H 3.23, N 17.94. Found: C 42.23, H 3.23, N 17.87.

Synthesis of $H_2C(3\text{-}CF_3\text{-}5\text{-}MePz)_2Re(CO)_3Br$ (2)

$H_2C(3\text{-}CF_3\text{-}5\text{-}MePf)_2$ (176.8 mg, 0.566 mmol) was added to a solution of $[Re(CO)_4Br]_2$ (202.2 mg, 0.267 mmol) in 10 mL THF, and refluxed overnight. The solvent was removed under vacuum, leaving a yellow precipitate, which was dissolved in a small quantity of CH_2Cl_2 and filtered through Celite. The filtrate was stored at -30 °C, resulting in the formation of ivory crystals. (213.0 mg, 57%).

Characterization: IR(CH_2Cl_2): 2045 (vs), 1943 (vs), 1920 (vs) νCO. MS, +ve FAB (m/e, rel. int.): M^+ (662, 21), M-CO^+ (634, 8), M-2CO^+ (606, 1), M-Br^+ (583, 57), M-3CO^+ (578, 15). ^1H NMR (CD_2Cl_2): δ 2.59 (d, 6H, $^4J_{H-H}$ = 0.4 Hz), 6.04 (d, 1H, $^1J_{H-H}$ = 15 Hz), 6.74 (q, 2H), 8.78 (d, 1H). ^{19}F NMR (CD_2Cl_2): δ -59.89 (s, 6F), -63.59 (s, 3F). ^{13}C APT NMR (CD_3NO_2): δ 11.95 (s,

CH_3), 58.89 (s, CH_2), 110.03 (s, CH). Anal. Calcd for $C_{14}H_{10}N_4F_6O_3BrRe$: C 25.39, H 1.52, N 8.46, Br 12.06. Found: C 25.44, H 1.55, N 8.02, Br 12.27.

Synthesis of $Re(CO)_3(PMe_3)_2Br$ (3)

To $H_2CPf_2Re(CO)_3Br$ (30 mg, 75.5 μmol) in 20 mL CH_2Cl_2 was added PMe_3 (7.8 μL, 75.4 μmol). The solution was stirred for approximately 20h, at which time the infrared indicated that the reaction had not gone to completion. An additional 7.8μL of PMe_3 was added, and stirred for an additional 2h. The solution was concentrated, layered with hexanes, and stored at -30°C. A tan colored precipitate was isolated.

Characterization: IR ($CHCl_3$): 2032 (s), 1950 (s), 1986 (s) νCO. MS, 220 °C/70 eV (m/e, rel. int.): M^+ (502, 23), $M\text{-}CO^+$ (474, 46), $M\text{-}2CO^+$ (446, 75), $M\text{-}3CO^+$ (417, 21).

Synthesis of $Re(CO)_3(PMe_2Ph)_2Br$ (4)

To a solution of $H_2CPf_2Re(CO)_3Br$ (27.2 mg, 41.1 μmol) in 20 mL THF was added dropwise a solution of PMe_2Ph (0.33 mL, 232 μmol) in 10 mL THF until no starting material could be seen in the IR. (approximately 2.5 mL of the PMe_2Ph solution was added) The solvent was removed under vacuum, leaving behind a white/yellow crystalline solid. This was dissolved in CH_2Cl_2, layered with hexanes, and stored at -26 °C. A sand colored precipitate formed.

Characterization: IR ($CHCl_3$): 2033 (s), 1953 (s), 1899 (s) νCO. MS, 230 °C/70 eV (m/e, rel. int.): M^+ (626, 21), $M\text{-}CO^+$ (598, 58), $M\text{-}2CO^+$ (570, 82), $M\text{-}Br^+$ (547, 15).

X-Ray Structure of $H_2CPf_2Re(CO)_3Br$ (2)

The X-ray crystallographic study was carried out by Dr. R. McDonald of the Structure Determination Laboratory of this Department. This section and the tables are adapted from his report.

Suitable crystals of **2** were grown by the slow evaporization of CH_2Cl_2 at room temperature. A crystal of dimensions 0.24 x 0.21 x 0.20 mm was obtained, having a $P2_1/m$ space group.

The structure was solved using a three dimensional Patterson synthesis which gave the positional parameters for the Re atom. The remaining non-hydrogen atoms were located by the usual combination of least squares refinement and difference Fourier synthesis.

Refinement of atomic parameters were carried out by full matrix least-squares techniques on F_o minimizing the function

$$\Sigma w \, (|F_o| - |F_c|)^2$$

and the weighting factor w is given by

$$w = 4F_o^{\,2} / \sigma^2(F_o)^2$$

All hydrogen atoms were included at their idealized calculated distances, assuming C-H distances of 0.94 Å.

In the final cycle, 139 parameters were refined using 1738 observations having I>2σ(I). The final agreement factors were:

$$R_1 = \Sigma | F_o| - |F_c| \; / \; \Sigma | F_o| \; = \; 0.0322$$

$$R_2 = [\, \Sigma w \, (| F_o| - |F_c| \,)^2 \; / \; \Sigma w \, F_o^2 \;]^{1/2} \; = \; 0.0794.$$

Table 2-4. Crystal Data and Details of Structure Refinement for $H_2CPf_2Re(CO)_3Br$

A. Crystal Data

$C_{14}H_{10}BrF_6N_4O_3Re$; FW = 662.37
Crystal dimensions (mm): 0.24 X 0.21 X 0.20
monoclinic space group $P2_1/m$ (No. 11)
a (Å) = 7.3483(10) b (Å) = 14.660(2) c (Å) = 8.8043(7)
V(Å^3) = 941.8(2) Z = 2 r_{calcd} (Mg/m^3) = 2.336 μ (mm^{-1}) = 8.654

B. Data Collection and Refinement Conditions

Radiation (*l* [Å])	Mo K*a* (0.71073)
F_{000}	620
Data collection *q* range (deg)	2.33 to 25.00
Index ranges	$-1 \le h \le 8, -1 \le k \le 17, -10 \le l \le 10$
Reflections collected	2346
Independent reflections	1738 (R_{int} = 0.0273)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1738/0/139
Goodness-of-fit on F^2	1.082
Final R indices ($I > 2s(I)$)	R_1 = 0.0322, wR_2 = 0.0794
R indices (all data)	R_1 = 0.0367, wR_2 = 0.0819
Largest diff. peak and hole (e Å^{-3})	.952 and -1.015

Table 2-5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $H_2CPf_2Re(CO)_3Br$

Atom	*x*	*y*	*z*	U_{eq}
Re	-1175(1)	2500	-7242(1)	38(1)
Br	-3522(1)	2500	-5167(1)	59(1)
F(11)	2108(7)	603(4)	-8696(5)	90(2)
F(12)	-541(6)	194(4)	-8338(5)	76(1)
F(13)	1709(9)	-641(3)	-7566(6)	93(2)
O(1)	1008(13)	2500	-9956(8)	88(3)
O(2)	-3838(8)	1160(4)	-8981(7)	86(2)
N(11)	695(6)	1490(3)	-5884(5)	38(1)
N(12)	1459(6)	1685(3)	-4448(5)	38(1)
C(1)	241(14)	2500	-8877(10)	54(2)
C(2)	-2802(9)	1636(5)	-8310(7)	56(2)
C(10)	897(12)	2500	-3695(8)	43(2)
C(11)	1166(8)	226(5)	-7700(7)	51(2)
C(12)	1431(8)	682(4)	-6187(7)	43(1)
C(13)	2638(8)	375(4)	-4960(7)	47(1)
C(14)	2648(7)	1033(4)	-3861(6)	42(1)
C(15)	3752(8)	1106(5)	-2328(6)	54(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2-6. Bond Lengths (Å) for $H_2C(Pf)_2Re(CO)_3Br$

Re–C(1)	1.874(9)	F(13)–C(11)	1.332(9)	N(12)–C(10)	1.451(6)
Re–C(2)	1.911(7)	O(1)–C(1)	1.161(11)	C(11)–C(12)	1.483(8)
Re–N(11)	2.263(5)	O(2)–C(2)	1.144(8)	C(12)–C(13)	1.389(8)
Re–Br	2.6569(10)	N(11)–C(12)	1.341(8)	C(13)–C(14)	1.366(8)
F(11)–C(11)	1.303(7)	N(11)–N(12)	1.351(6)	C(14)–C(15)	1.494(7)
F(12)–C(11)	1.313(7)	N(12)–C(14)	1.355(7)		

Table 2-7. Bond Angles (deg) for $H_2C(Pf)_2Re(CO)_3Br$

C(1)–Re–C(2)	89.7(3)	O(2)–C(2)–Re	176.0(7)
C(2)′–Re–C(2)	83.0(4)	N(12)–C(10)–N(12)′	111.0(6)
C(2)–Re–N(11)′	177.5(2)	F(11)–C(11)–F(12)	106.5(6)
C(1)–Re–N(11)	92.8(3)	F(11)–C(11)–F(13)	106.7(6)
C(2)–Re–N(11)	97.5(2)	F(12)–C(11)–F(13)	105.4(6)
N(11)′–Re–N(11)	81.8(2)	F(11)–C(11)–C(12)	112.9(6)
C(1)–Re–Br	173.3(3)	F(12)–C(11)–C(12)	114.6(5)
C(2)–Re–Br	85.4(2)	F(13)–C(11)–C(12)	110.1(5)
N(11)–Re–Br	92.28(10)	N(11)–C(12)–C(13)	111.5(5)
C(12)–N(11)–N(12)	103.9(4)	N(11)–C(12)–C(11)	124.3(5)
C(12)–N(11)–Re	135.0(4)	C(13)–C(12)–C(11)	123.8(6)
N(12)–N(11)–Re	121.0(3)	C(14)–C(13)–C(12)	105.7(5)
N(11)–N(12)–C(14)	112.6(5)	N(12)–C(14)–C(13)	106.2(5)
N(11)–N(12)–C(10)	119.5(5)	N(12)–C(14)–C(15)	123.4(6)
C(14)–N(12)–C(10)	127.8(5)	C(13)–C(14)–C(15)	130.3(6)
O(1)–C(1)–Re	175.4(9)		

Primed atoms are related to unprimed ones via the symmetry transformation $x, {}^{1}/2-y, z$.

REFERENCES

1. (a). Trofimenko, S. *Acc. Chem. Res.* **1971**, *4*, 17.

   (b). Trofimenko, S. *Chem. Rev.* **1972**, *72*, 497.

   (c). Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115.

   (d). Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.

2. Trofimenko, S. *J. Am. Chem. Soc.* **1970**, *92*, 5118.

3. Krentz, R. PhD Thesis, University of Alberta, 1989, Chapter 3.

4. (a). Trofimenko, S. *Inorg. Chem.* **1970**, *9*, 2493.

   (b). Kosky, C. A.; Ganis, P.; Avitabile, G. *Acta. Cryst.* **1971**, *B27*, 1859.

   (c). Cotton, F. A.; Day, V. W. *J. Chem. Soc., Chem. Commun.* **1974**, 415.

   (d). Trofimenko, S. Prog. *Inorg. Chem.* **1986**, *34*, 115.

   (e). Cotton, F. A.; LaCour, T.; Stanislowski, A. G. *J. Amer. Chem. Soc.* **1974**, *96*, 754.

5. (a). Wright, J. B.; W. E. Dulin; Markillie, J. H. *J. Med. Chem.* **1964**, *7*, 102.

   (b). Nishiwaki, T. *J. Chem. Soc. (B)*, **1967**, 885.

   (c). Fields, R; Tomlinson, J. P. *J. Fluor. Chem.* **1979**, *13*, 147.

6. McCurdy, W. H. *Inorg. Chem.* **1975**, *14*, 2292.

7. Paudler, W. W. *Nuclear Magnetic Resonance*, John Wiley and Sons: Toronto, 1987, pg 81-82.

8. Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

9. (a). Angelici, R. J.; Basolo, F.; Poe, A. J. *J. Am. Chem. Soc.* **1963,** *85,* 2215.

   (b). Booth, B. L.; Haszeldine, R. N. *J. Chem. Soc. (A)* **1966,** 157.)

10. March, J. *Advanced Organic Chemistry, 3th Edition,* John Wiley and Sons: Toronto, 1984, pg 124-128.

11. Cobbledick, R. E.; Dowdell, L. R. J.; Einstein, F. W. B.; Hoyano, J. K.; Peterson, L. K. *Can. J. Chem.* **1979,** *57,* 2285.

12. Gan, L-B. PhD Thesis, University of Alberta, 1990.

13. (a). Herring, F. G.; Patmore, D. J.; Storr, A. *J. Chem. Soc., Dalton Trans.* **1975,** 711.

    (b). Louie, B. M.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1984,** *62,* 1057.

    (c). Nussbaum, S.; Storr, A. *Can. J. Chem.* **1985,** *63,* 2550.

14. Louie, B. M.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1985,** *63,* 503.

15. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds, Fourth Edition,* John Wiley and Sons: Toronto, 1981, p. 206.

16. Shiu, K-B.; Chang, C-J.; Wang, S-L.; Liao, F-L. *J. Organomet Chem.* **1991,** *407,* 225.

17. Reimann, R. H.; Singleton, E. *J. Organomet. Chem.* **1973,** *59,* 309.

18. (a). Lobbia, G. G.; Cingolani, A.; Leonesi, D.; Lorenzotti, A.; Bonati, F. *Inorg. Chim. Acta* **1987,** *130,* 203.

    (b). Lobbia, G. G.; Bonati, F. *J. Organomet. Chem.* **1989,** *366,* 121.

19. Mukerjee, S.L.; Nolan, S. P.; Hoff, C. D.; Lopez de la Vega, R. *Inorg. Chem.* **1988**, *27*, 81.

20. Abel, E. W.; Hargreaves, G. B.; Wilkinson, G. *J. Chem Soc.* **1958**, 3149.

CHAPTER 3

SYNTHESIS AND REACTIVITY OF $HBPf_3Re(CO)_3$

Section 1

INTRODUCTION

Since their introduction in 1967, pyrazolylborates[1] have been used to synthesize compounds of nearly all the transition metals.[2] Due primarily to their large size, they have been instrumental in providing stability to otherwise sensitive compounds, creating enzyme models and anchoring the metal to provide support while performing reactions on the complex's other coordination sites.[2d]

Comparisons of the chemistry of the cyclopentadienyl (Cp) and pentamethylcyclopentadienyl (Cp*) ligands to that of the pyrazolylborate ligand are of interest, as they provide the opportunity to study the effect of the steric and electronic components of the pyrazolylborate on the metal center. As the 3-, 4- and 5-positions of the pyrazoles are altered (Figure 1-2), so are the steric and electronic properties of the pyrazolylborate. This is one of the main tenets of Trofimenko's "second generation" pyrazolylborates.[3]

The (3-trifluoromethyl-5-methylpyrazol-1-yl)borate ($HBPf_3$) ligand was synthesized in this group by Richard Krentz,[4] and has exhibited interesting properties. On rhodium centers, it has altered the usual relative thermochemical stability of hydridovinyl and η^2-ethylene complexes, and it has activated the C-H bonds in benzene and cyclohexane, as well as the Si-H bond in $HSiR_3$ (R=Cl, Me).[4b] Consequently, the use of $HBPf_3$ on other metal centers was of interest.

Although pyrazolylborate chemistry on Group six metals has been extensively investigated, very little focus has been placed on those in Group seven, especially rhenium. Due principally to their commercial availability, most investigations have involved only the $HBPz_3$ and $HBPz^*{}_3$ ligands. Therefore, using the $HBPf_3$ ligand provided the opportunity to compare its steric and electronic differences to that of the other two pyrazolylborates.

The syntheses[5] and crystal structures[6] of $HBPz_3Re(CO)_3$ and $HBPz^*{}_3Re(CO)_3$ have been reported. Therefore, a structure of $HBPf_3Re(CO)_3$ would aid in determining the extent that steric effects play in its chemistry as compared to the other two ligands. Also, the reactivity of pyrazolylboraterhenium tricarbonyl complexes differs from that of the Cp analogues. For instance, the reaction of $CpRe(CO)_3$ with Br_2 yielded the seven-coordinate $CpRe(CO)_2Br_2$ complex.[7] However, when bromine is reacted with the $HBPz^*{}_3$ analogue, bromination at the 4-position of the pyrazole results.[5b] While steric effects may prevent the formation of the seven-coordinate pyrazolylborate complex, some other property may also account for the unusual substitution reaction observed. The presence of the electron-withdrawing CF_3 group in the 3-position of the $HBPf_3$ ligand may provide insight into the chemistry observed.

Previous rhenium chemistry using the $HBPz_3$ and $HBPz^*{}_3$ ligands has mainly involved the photochemistry of the tricarbonyl complex.[5a,6b] Photolysis in a coordinating solvent (tetrahydrofuran) has resulted in the substitution of one carbonyl with a solvent molecule, while subsequent chemistry has demonstrated the facile substitution of the solvent ligand with various other donor ligands. Consequently, the photochemistry of $HBPf_3Re(CO)_3$, and its subsequent reactions with PPh_3 and PMe_3 has been studied in this work. Stable seventeen-electron paramagnetic species have also been synthesized by reacting the THF adduct with Br_2 and CCl_4. Their effective magnetic moments have been measured and will be presented.

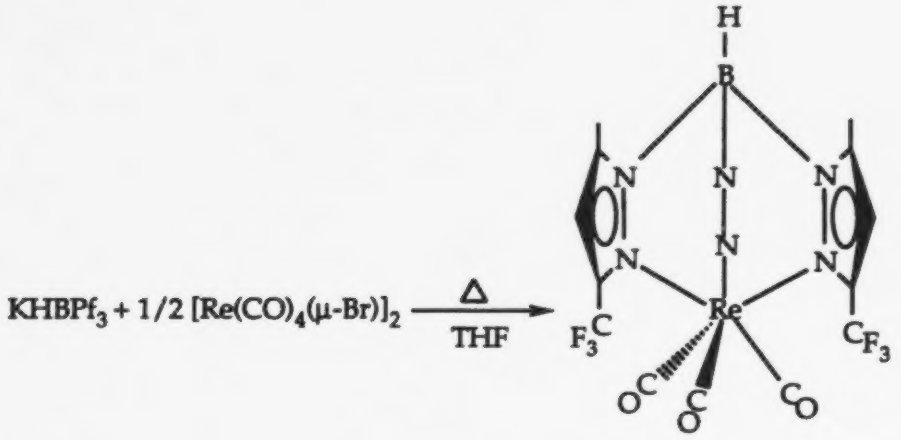
Section 2

SYNTHESIS AND PROPERTIES OF $HBPf_3Re(CO)_3$ (5)

The preparation of 3-trifluoromethyl-5-methylpyrazole (HPf) was first reported[8] in 1964. However, its use in synthesizing the tris(3-trifluoromethyl-5-methylpyrazol-1-yl)borate ligand ($HBPf_3$) was not reported until 1989 by Graham and Krentz.[4] The reaction leading to the $HBPf_3$ ligand is regiospecific: all three CF_3 groups occupy the same position in the borate ligand. That position was shown by X-ray crystallography to be the 3-position,[4b] which appears consistent with McCurdy's speculation of the formation of a less sterically-hindered transition state.[9] Attempts to purify the ligand have been only partly successful, therefore, for reaction purposes, an excess is used.

The preparation of 5 was similar to McCleverty's synthesis of the $HBPz^*_3$ analogue.[5b] A tetrahydrofuran solution containing $KHBPf_3$ and $[Re(CO)_4(\mu\text{-}Br)]_2$ was refluxed until starting material bands had disappeared, and new bands at 2044 and 1937 cm^{-1} were present. The solvent was removed and the oily residue washed with methanol, yielding $HBPf_3Re(CO)_3$ as a white, microcrystalline precipitate, in low yield (equation (3-1)).

The carbonyl stretching frequencies of 5 are approximately 20 and 30 wavenumbers higher than each νCO value found in $HBPz_3Re(CO)_3$ and $HBPz^*_3Re(CO)_3$ respectively. This suggests that the $HBPf_3$ ligand is less electron-donating to the metal center, presumably due to the presence of the electron-withdrawing CF_3 groups on the pyrazole ring. Proton and fluorine NMR are indicative of a compound with C_{3v} symmetry as the ^1H spectrum contains only two singlets, one for the 5-Me group and one for the 4-H proton, while there is only a singlet in the ^{19}F spectrum.



5

(3-1)

The synthesis of $HBPz^*{}_3Re(CO)_3$ using $[Re(CO)_4(\mu\text{-}Cl)]_2$[5b] and $[Re(CO)_4(\mu\text{-}Br)]_2$[6b] resulted in the formation of the by-products $(HPz^*)_2Re(CO)_3Cl$[5b] and $(OMe)_2B(Pz^*)_2Re(CO)_3$[6b] respectively. McCleverty[5b] postulated that the formation of the rhenium chloride product may have resulted from the decomposition of the $HBPz^*{}_3$ ligand by some rhenium species formed in solution. However, Gan[6b] only observed the dimethoxide complex, and speculated that while it may have formed from the decomposition of the pyrazolylborate ligand, it may also have resulted from the substitution of the two hydrogens attached to boron in $H_2B(Pz^*)_2$, which was present as an impurity in the $HBPz^*{}_3$ ligand.

In the preparation of 5, other infrared bands were noted in the 2200 - 1600 cm^{-1} region. Attempts to isolate these products using the methods employed by McCleverty and Gan were unsuccessful. Addition of chloroform did afford a white precipitate, but it appeared to be the result of decomposition as its infrared spectrum exhibited six carbonyl stretching bands and the ^1H and ^{19}F NMR contained numerous peaks, among which only unreacted $KHBPf_3$ was identified.

X-Ray Structure of $HBPf_3Re(CO)_3$ (5)

The crystal structures of the $HBPz_3Re(CO)_3$ and $HBPz^*{}_3Re(CO)_3$ complexes have already been determined.[6] Therefore, a structure of the $HBPf_3Re(CO)_3$ analogue would provide the opportunity to compare the ligands. Table 3-1 compares some bond length and angle values for the analogous $HBPz_3$ and $HBPz^*{}_3$ ligand to that of **5**. In most cases, it appears that similar values are present in the three complexes.

Table 3-1. Comparisons of Crystal Structure Data for $HBPz_3Re(CO)_3$, $HBPz^*{}_3Re(CO)_3$ and $HBPf_3Re(CO)_3$*

Bond/Angle	$HBPz_3Re(CO)_3$	$HBPz^*{}_3Re(CO)_3$	$HBPf_3Re(CO)_3$
M-CO_{avg} (Å)	1.82(3)	1.911(5)	1.909(7)
M-N_{avg} (Å)	2.22(2)	2.172(3)	2.217(6)
N-N_{avg} (Å)	1.38(3)	1.387(5)	1.360(8)
3-C-4-C (Å)	1.38(4)	1.399(7)	1.391(9)
5-C-4-C (Å)	1.37(4)	1.386(7)	1.368(9)
N(11)-Re-C(1) (°)	91.7(9)	95.0(2)	93.8(2)
Re-C-O_{avg} (°)	175(2)	176.8(5)	177.3(7)

* average values were determined by taking into account all bonds present

The molecular structure of **5**, shown in Figure 3-1, may be described as a slightly distorted octahedron with C_{3v} symmetry. This is consistent with spectroscopic data. Coincidentally, a crystallographic mirror plane includes

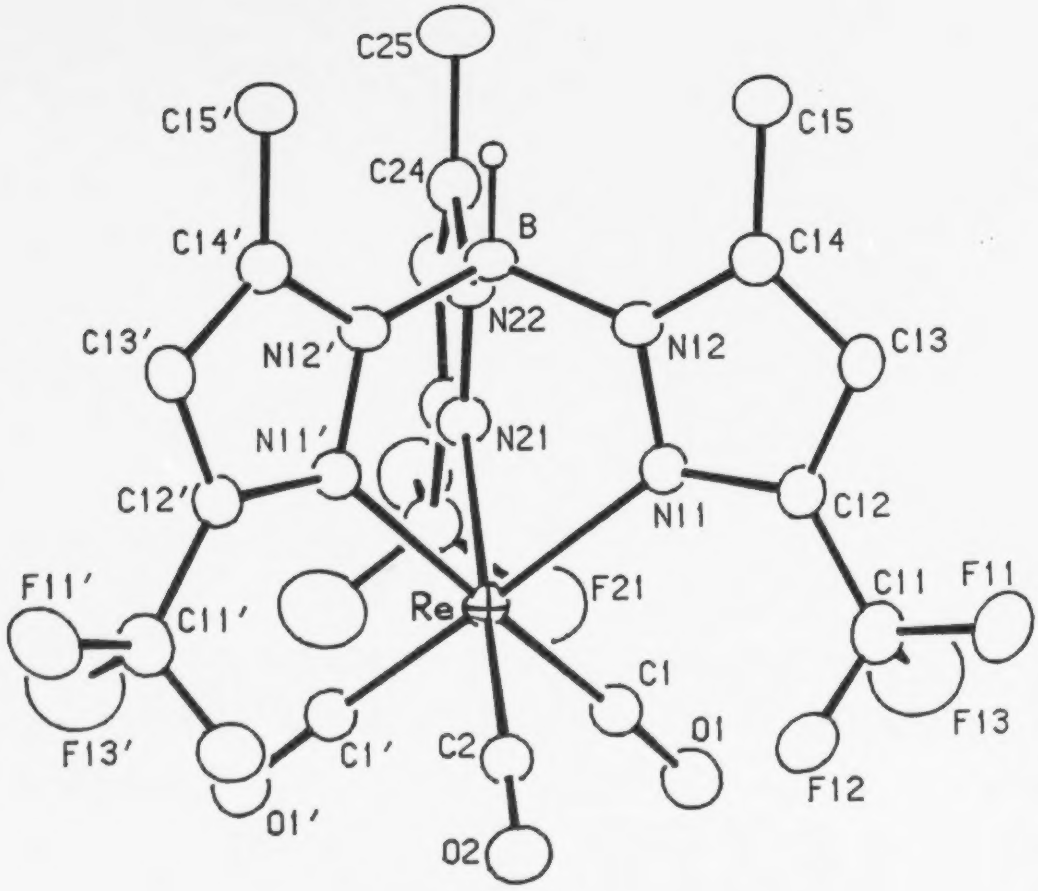

C25
C15'
C15
C24
B
C14'
C14
N22
C13'
N12'
N12
C13
N11'
N21
C12'
N11
C12
F11'
C11'
Re
F21
C11
F11
C1
F13
F13'
C1'
C2
O1
O1'
F12
O2

Figure 3-1. ORTEP view of $HBPf_3Re(CO)_3$ (5)

the metal center, one Pf group, and one carbonyl. Symmetry related atoms are assigned the "prime" value. Although the $HBPf_3$ ligand can be bidentate in some cases,[4b] it is tridentate here , allowing the complex to satisfy the 18 electron rule.

As with the $HBPz^*_3$ analogue[6] the rhenium center is within the pocket made by the presence of the CF_3 groups in the 3-position on the pyrazole rings. This illustrates one important feature of pyrazolylborate chemistry which is not found with the planar cyclopentadienyl rings.

The Re-N_{avg} bond length for 5 is 2.217(6)Å, which is similar to the value obtained in the $HBPz_3Re(CO)_3$ analogue (2.22(2)Å) but longer than the value in the $HBPz^*_3Re(CO)_3$ complex (2.174(6)Å). The bond length variances may be related to the electron richness of the pyrazolylborates.

Bond angles between the carbonyls and the trans pyrazole for 5 are 178.1(2) and 176.9(3)^o, which are consistent with values obtained for $HBPz^*_3Re(CO)_3$ (176.7(2), 178.7(2)^o) and close to values for $HBPz_3Re(CO)_3$ (171.9(9), 171.2(9), 167.9(8)^o).

Section 3

THE REACTIVITY OF $HBPf_3Re(CO)_3$ (5)

Photolysis

Photolysis of 5 in tetrahydrofuran results in the loss of one CO and the coordination of one solvent molecule to form $HBPf_3Re(CO)_2THF$ (6). During the photolysis, the colorless solution of 5 turns yellow-orange. Although attempts to determine the species responsible for this coloration have failed, it has been suggested[6b] that it is due to decomposition products, as 6 and the corresponding $HBPz_3$ and $HBPz^*_3$ analogues are light yellow.

The infrared spectrum of the tetrahydrofuran solution exhibits two carbonyl stretching bands, at 1934 and 1855 cm^{-1}, which are approximately 80 cm^{-1} below that found in 5. This indicates increased electron donation from the metal center to the carbonyl ligands, decreasing the bond order of the C-O bond. This would be the result of the donation of electrons through the oxygen in the THF molecule, which is not a π-acceptor ligand. The ^1H spectrum exhibits peaks in a 2:1 ratio for the 5-Me protons and two unresolved peaks (also in a 2:1 ratio) for the 4-H protons on the pyrazole ring, while the ^{19}F NMR contains only a singlet. Although peaks in a 2:1 ratio would be expected in the ^{19}F NMR, the singlet is probably a result of coincidentally overlapping peaks.

Interestingly, if the solutions of 5 are similar to those for the $HBPz^*_3Re(CO)_3$ analogue, the time for the reaction to occur is substantially increased, and more starting material is left intact. For example, a 1.68 mM THF solution of 5 required a photolysis time of over three hours, and only 85% conversion was obtained before excessive decomposition of product occurred. However, for the $HBPz^*_3Re(CO)_3$ analogue,[6b] a 2.64 mM THF solution required only 20 minutes for the reaction to go to completion. The $HBPz_3$ analogue[5a] required less time to form when using a weaker source. This would imply higher internal filtering, caused by the formation of the yellow-orange solution formed in synthesizing 6, compared to the $HBPz^*_3$ and $HBPz_3$ analogues.

Halogenation

The reactivity of 5 is unique in that the direct reaction with bromine did not substitute any of the CO ligands, and did not substitute the 4-H proton of the pyrazole ring. When the HBPz*$_3$ ligand was used, no substitution of the carbonyls was observed, but the 4-H on the pyrazolylborate ligand was substituted by the halide.[5b] Two explanations could account for such behavior. The HBPf$_3$ ligand contains substituents at both the 3- and 5-positions, as does the HBPz*$_3$ ligand. However, if the CF$_3$ group is slightly larger in size than the methyl substituent, the steric difference could inhibit the approach of bromine. Secondly, the charge around the pyrazole ring is different for the HBPf$_3$ ligand than for the other two. Figure 3-1 illustrates the various partial charges on the carbon atoms of the pyrazole rings due to the presence of more electronegative atoms. For Pz and Pz*, the charge on the 4-carbon is slightly negative, while the 4-C in Pf

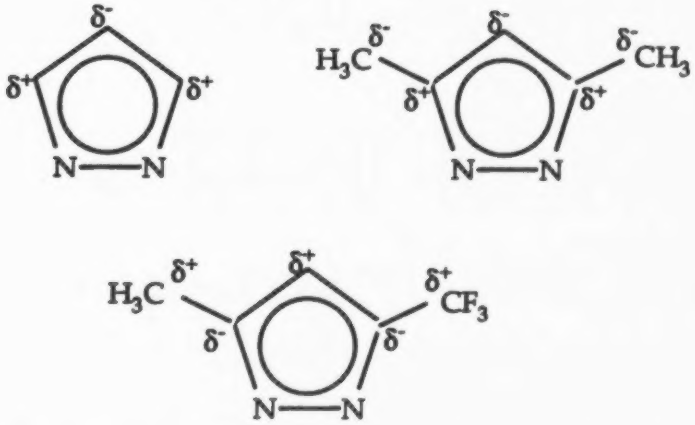


Figure 3-2. Partial Charges on Carbon Atoms in Pz, Pz* and Pf

has a slightly positive charge. This difference in partial charges could affect the substitution of the 4-H by bromine, although the mechanism of that substitution is not known.

C-H Activation Attempts

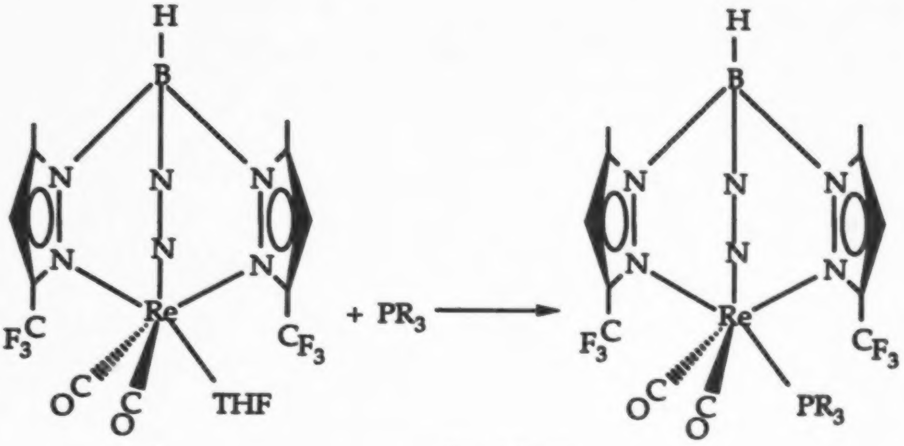
Attempts to observe C-H activation by photolysis of 5 in benzene, were unsuccessful. After several hours, the reactant bands had disappeared, but no new product bands were present in the 2200 - 1600 cm^{-1} region of the infrared. It has been suggested that for $HBPz^{*}_3Re(CO)_3$, the positioning of the seventh ligand would cause a large steric interaction with the 3-substituent on the pyrazolylborate ligand.[6b] Since the CF_3 substituent in the 3-position on the pyrazoles in $HBPf_3$ ligand is similar in size to CH_3, this result is not surprising.

Section 4

THE REACTIVITY OF $HBPf_3Re(CO)_2(THF)$ (6)

The photolysis of 5 in tetrahydrofuran led to the formation of the THF adduct 6, and this THF solution was used, without purification, for subsequent reactions. The analogous $HBPz_3$ and $HBPz^{*}_3$ complexes have demonstrated that the lability of the THF ligand provides a substitution pathway for a variety of interesting complexes.[5a,6b] This has also been found for 6.

It was expected that the reaction of **6** with PMe_3 and PPh_3 would result in the substitution of the THF ligand, as was observed for the $HBPz_3$[5a] and $HBPz^*_3$[6b] analogues (equation (3-2)). Although the PMe_3 complex could be made with stirring over three days, a similar reaction time saw no change in the infrared spectrum for the PPh_3 reaction. Even after refluxing for 24h, little change was observed.



(3-2)

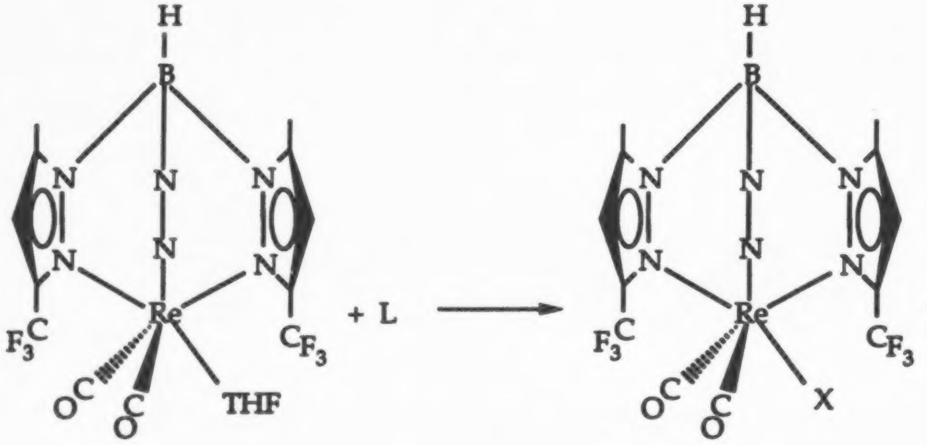
6

R = Me **7**
Ph, no reaction

This difference may be a consequence of the sizes of the pyrazolylborate ligands. Due to the presence of substituents in the 3- and 5-positions of the pyrazoles in $HBPf_3$, its cone angle would be larger than the 180° value for $HBPz_3$, and similar to the 224° value for $HBPz^*_3$. Considering that the Tolman cone angle[10] for PMe_3 is 118° while that for PPh_3 is 145°, the steric difference created by substituting the CH_3 and CF_3 groups found in the 3-position of the $HBPz^*_3$ and $HBPf_3$ ligands can be rationalized.

Synthesis of Paramagnetic Complexes

Although no reaction was observed between 5 and bromine, the reaction of 6 with CCl_4 and Br_2 resulted in the substitution of THF with Cl or Br, thereby forming seventeen-electron radicals, in fair yield (equation (3-3)). As was stated in Chapter 1, paramagnetic complexes do not normally provide useful NMR spectra, due to broadened signals. Through the use of Evans' method,[11] it is possible to determine by NMR techniques the magnetic moment of a compound, from which the number of unpaired electrons may be inferred.



(3-3)

6

L = CCl_4
Br_2

X = Cl 8
Br 9

Both 8 and 9 may be left in air for several days without appreciable changes in their color or infrared spectrum. The stability added to unsaturated and radical complexes by coordination of the trispyrazolylborate ligand has been demonstrated and attributed to the size of the ligand.[12] Chapter 4 will describe an air- and moisture-stable seventeen-electron radical, as well as sixteen-electron molybdenum complexes. These also exhibit remarkable stability, presumably due to the inability of other ligands to approach the metal center.

Two mechanisms for the formation of $HBPz^*_3Re(CO)_2Cl$ from the reaction of $HBPz^*_3Re(CO)_2THF$ and CCl_4 have been postulated,[6b] and may well apply to the formation of $HBPf_3Re(CO)_2Cl$. These are shown in Scheme 3-1.

$$HBPz^*_3Re(CO)_2THF + CCl_4 \longrightarrow HBPz^*_3Re(CO)_2ClCCl_3 + THF$$

$$HBPz^*_3Re(CO)_2ClCCl_3 \longrightarrow HBPz^*_3Re(CO)_2Cl + CCl_3^{\cdot}$$

(a)

$$HBPz^*_3Re(CO)_2THF + CCl_4 \longrightarrow [HBPz^*_3Re(CO)_2THF]^+ + CCl_4^{\cdot -}$$

$$CCl_4^{\cdot -} \longrightarrow Cl^- + CCl_3^{\cdot}$$

$$Cl^- + [HBPz^*_3Re(CO)_2THF]^+ \longrightarrow HBPz^*_3Re(CO)_2Cl$$

(b)

Scheme 3-1. Possible Mechanisms for Rhenium Radical Formation

Although the dichloro- and dibromocarbonyl products were also formed when $HBPz^*_3Re(CO)_2THF$ reacted with CCl_4 and Br_2,[6b] no such product was observed in similar reactions with 6. It has been suggested[6b] that of the two proposed mechanisms, only (b) can account for the formation of these dihalogenated species by further oxidation using CCl_4. Therefore, either the $HBPf_3$ ligand is too large to accomodate the two bromides or CCl_4 is unable to further oxidize 8 or 9 to form the dihalogenated species.

Effective magnetic moments were measured for $HBPf_3Re(CO)_2X$ (X=Cl, Br) and are compared to analogous complexes synthesized by Gan[6b] in Table 3-2. For spin-only magnetic moments with one unpaired electron, values close to 1.73 BM would be obtained, which is close to the values obtained for 8 (2.02 BM) and 9 (1.94 BM) and consistent with Gan's findings. A more detailed calculation for the magnetic moment is provided in the Experimental Section.

Table 3-2. Magnetic Moments of Paramagnetic Compounds 8 and 9[a]

Complex	Mass (mg)	Volume (mL)	$\Delta\nu$ (Hz)	χ_{dia} ($\times 10^6$) ($cm^3 mol^{-1}$)	μ_{eff} (BM)
$HBPf_3Re(CO)_2Cl$ (8)	9.0	0.80	18.85	-193.71	2.02
$HBPf_3Re(CO)_2Br$ (9)	5.0	0.80	9.25	-204.21	1.94
$HBPz^*_3Re(CO)_2Cl$[b]					2.20
$HBPz^*_3Re(CO)_2Br$[b]					2.37

a. All spectra were run on a 300 MHz FT NMR at 25 °C with cyclohexane as reference.
b. See reference 6b.

Section 5

EXPERIMENTAL

All reactions were carried out under an inert atmosphere of prepurified argon, using standard Schlenk techniques. $[Re(CO)_4(\mu\text{-}Br)]_2$ was synthesized according to literature methods.[13] Complexes showed oxygen sensitivity in solution, but solids could be handled in air for prolonged periods of time without decomposition.

Synthesis of $HBPf_3Re(CO)_3$ (5)

$KHBPf_3$ (520 mg, 1.04 mmol) was added to a solution of $[Re(CO)_4(\mu\text{-}Br]_2$ (236 mg, 0.312 mmol) in 100 mL THF, and the solution refluxed overnight. The solvent was removed on the rotary evaporator, leaving behind a yellow oil. Methanol was added (3 x 10 mL) and the solution stirred. This yielded a white precipitate. (121 mg, 27%)

Characterization: IR (cyclohexane): 2051 (w), 1950 (w); (CH_2Cl_2): 2045 (vs), 1937 (vs) νCO. MS, 200 °C/70 eV (m/e, rel. int.): M^+ (730, 51), $M\text{-}CO^+$ (702, 33), $M\text{-}2CO^+$ (674, 9), $M\text{-}3CO^+$ (646, 24). ^1H NMR (CD_2Cl_2): δ 2.49 (s, 9H), 6.45 (s, 3H). ^{19}F NMR (CD_2Cl_2): δ -59.46 (s, 9F). Anal. Calcd for $C_{18}H_{13}N_6F_9ReO_3B$: C 29.64, H 1.80, N 11.52. Found: C 29.52, H 2.00, N 11.22.

Synthesis of $HBPf_3Re(CO)_2THF$ (6)

$HBPf_3Re(CO)_3$ (220 mg, 0.302 mmol) in 180 mL THF was photolyzed using a high pressure mercury lamp (450 watts) with a Pyrex filter. After 3 hours, the reaction had gone to ~ 85% completion, and the originally colorless solution had become yellow-orange. Further photolysis resulted in the formation of a dark yellow-green solution whose infrared spectrum no longer exhibited product peaks. The solution was concentrated and hexanes were added, affording a precipitate. The solution was filtered and the solid washed with hexanes (3 x 5 mL) giving a light yellow precipitate. (58 mg, 25%)

Characterization: IR (THF): 1934 (s), 1855 (s) νCO. MS, 200 °C/70 eV (m/e, rel. int.): M-THF$^+$ (702, 3), M-2CO$^+$ (646, 2). ^{1}H NMR (THF, d_8): δ 2.47 (s, 3H), 2.55 (s, 6H), 6.69 (s, 3H, contains unresolved shoulder). ^{19}F NMR (THF, d8): -59.77 (s, 9F). Anal. Calcd for $C_{21}H_{21}N_6F_9BReO_3$: C 32.60, H 2.72, N 10.87. Found: C 32.31, H 2.53, N 10.10.

Synthesis of HBPf$_3$Re(CO)$_2$(PMe$_3$) (7)

To a 50 mL aliquot of a freshly prepared solution of HBPf$_3$Re(CO)$_2$THF (made from a solution of 220 mg HBPf$_3$Re(CO)$_3$ in 180 mL THF) was added PMe$_3$ (0.094 mL, 0.908 mmol). The yellow solution was stirred for 3 days. The solvent was removed in vacuo, and the residue dissolved in a minimum of CH_2Cl_2. This was chromatographed on a 1 x 20 cm Florisil (Mesh 60-100) column using CH_2Cl_2. The solvent was removed under vacuum, and the residue washed with hexanes (3 x 10 mL). This was dried under vacuum and yielded a cream colored precipitate. (15 mg, 23% based on 5)

Characterization: IR (Hexanes): 1963 (w), 1889 (w) νCO. MS 200 °C/70 eV (m/e, rel. int.): M$^+$ (778, 100), M-CO$^+$ (750, 4), M-2CO$^+$ (72, 21), M-2CO-PMe$_3^+$ (646, 10). ^{1}H NMR (CD_2Cl_2): δ 1.43 (d, 9H, $^2J_{P\text{-}H}$= 7.5 Hz), 2.36 (s, 3H), 2.52 (s, 6H), 6.37 (s, 1H), 6.52 (s, 2H). ^{19}F NMR (CD_2Cl_2): -57.18 (s, 6F), -60.28 (s, 3F). Anal. calcd for $C_{20}H_{22}N_6F_9BRePO_2$: C 30.90, H 2.83, N 10.81. Found: C 31.20, H 3.10, N 9.75.

Preparation of $HBPf_3Re(CO)_2Cl$ (8)

To a freshly prepared solution of $HBPf_3Re(CO)_2THF$ (50 mL of a solution prepared from 220 mg 5 in 180 mL THF) was added CCl_4 (0.4 mL) and the solution was stirred for 2 days. The THF was removed under vacuum, leaving a yellow-orange precipitate. This was dissolved in CH_2Cl_2 and chromatographed on a 1 x14 cm Florisil column (60-100 mesh). The solution was concentrated, layered with hexanes and stored at -26 °C. A yellow precipitate settled out. (20 mg, 32% based on 5)

Characterization: IR (THF): 2024 (s), 1914 (s) νCO. MS, +ve FAB (m/e, rel. int.): M^+ (737, 2), $M\text{-}CO^+$ (709, 1), $M\text{-}Cl^+$ (701, 4), $M\text{-}2CO^+$ (681, 2). ^1H and ^{19}F NMR were not obtained due to the compounds paramagnetic character. Anal. Calcd for $C_{17}H_{13}N_6F_9BReClO_2$: C 27.70, H 1.77, N 11.41. Found: C 28.16, H 1.95, N 10.59. μ_{eff}: 2.02 BM (see below).

Preparation of $HBPf_3Re(CO)_2Br$ (9)

To a freshly prepared solution of **6** (75.8 mg of **5** in 150 mL THF) was added Br_2 (0.0143 mL, 44.2 mg, 0.277 mmol), and the solution allowed to stir until the infrared no longer contained bands indicating the presence of **6**. The solvent was removed in vacuo, leaving a brown residue. This was dissolved in CH_2Cl_2, and chromatographed on a 1 x 16 cm Florisil column (60-100 mesh). This solution was concentrated and layered with hexanes. An orange/brown precipitate formed, which was dried under vacuum. (26 mg, 32%, based on **5**). μ_{eff}: 1.94 BM (see below)

Characterization: IR (CH_2Cl_2): 2026 (s), 1919 (s) νCO. MS 220 °C/16 eV (m/e, rel. int.): M^+ (781, 29), M-CO^+ (753, 16), M-2CO^+ (725, 23), M-Br^+ (701, 2). ^1H and ^{19}F NMR were not obtained for this paramagnetic compound. Anal. Calcd for $C_{17}H_{13}N_6F_9BReBrO_2$: C 26.12, H 1.66, N 10.75. Found: C 26.37, H 1.64, N 9.99.

Calculation of Effective Magnetic Moment (μ_{eff})

While many methods for the determination of the effective magnetic moment[14] exist, only Evans' method[11] was used in this Chapter. A Wilmad Special Stem Coaxial Insert tube (196 mm - top 154 mm has OD (outer diameter) = 4 mm and the stem has an OD = 2 mm) containing 1% cyclohexane, as reference, in CD_2Cl_2 is placed inside a 178 mm (OD = 5 mm) NMR tube containing the sample, also dissolved in CD_2Cl_2, with 1% cyclohexane as reference. The following is a sample calculation for $HBPf_3Re(CO)_2Cl$ (**8**).

Using the 300 MHz NMR spectrometer, **8** (9.0mg) was dissolved in 0.80mL CD_2Cl_2. Two resonances were observed at 427.46 and 408.61 Hz, at 25 °C. Therefore, in determining the molar susceptibility, equation (1-2), m is 1.13x10-2 g/mL and Δv is 18.85 Hz. The mass susceptibility of the solvent χ_o is determined using Pascal's constants (Table 3-3), where $\chi_H = \chi_D$:

$$\begin{aligned}
&\text{H: } 2 \times (-2.93 \times 10^{-6}\ \text{cm3 mol}^{-1}) = -5.86 \times 10^{-6}\ \text{cm}^3\ \text{mo l}^{-1} \\
&\text{C: } 1 \times (-6.00 \times 10^{-6}\ \text{cm}^3\ \text{mol}^{-1}) = -6.00 \times 10^{-6}\ \text{cm}^3\ \text{mol}^{-1} \\
&\text{Cl: } 2 \times (-20.1 \times 10^{-6}\ \text{cm}^3\ \text{mol}^{-1}) = \underline{-40.2 \times 10^{-6}\ \text{cm}^3\ \text{mol}^{-1}} \\
&\qquad\qquad \chi_o\ (CD_2Cl_2) = -52.06 \times 10^{-6}\ \text{cm}^3\ \text{mol}^{-1}
\end{aligned}$$

χ_g (CD_2Cl_2) = -52.06×10^{-6} cm^3 mol^{-1} / 87 g mol^{-1} = -0.60×10^{-6} cm^3 g^{-1}

Neglecting the last term of equation (1-2) due to the dilute solutions used, and substituting in the above values gives:

$$\chi_g = \frac{3 \times 18.85}{2 \times 3.14 \times (300 \times 10^6) \times (1.13 \times 10^{-2})} - 0.60 \times 10^{-6}$$

$$= 2.06 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$$

$$\chi = 2.06 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1} \times 736.47 \text{ g mol}^{-1}$$

$$= 1.52 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$$

Using Pascal's constants, one can calculate the diamagnetic susceptibility of **8**. It was found to be -193.71×10^{-6} cm^3 mol^{-1}. Therefore,

$$\chi_{para} = \chi - \chi_{dia}$$

$$= 1.52 \times 10^{-3} - (-193.71 \times 10^{-6})$$

$$= 1.71 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$$

Now, the effective magnetic moment is calculated:

$$\mu_{eff} = 2.828 \times ((1.71 \times 10^{-3}) \times 298)^{0.5}$$

$$= 2.02 \text{ BM}$$

Table 3-3. Pascal's Constants

Atom	χ_A (x 10^{-6} cm^{-3} mol^{-1})	Atom	χ_A (x 10^{-6} cm^{-3} mol^{-1})
H	-2.93	F	-6.3
C	-6.00	Cl	-20.1
C (aromatic)	-6.24	Br	-30.6
N (aromatic)	-4.61	Re	67.6
B	-6.7	Mo	89.0
CO	-9.8		

X-ray Crystal Data of $HBPf_3Re(CO)_3$ (5)

The X-ray crystallographic determination was carried out by Dr. R. McDonald of this Department. The following details are adapted from his report.

A suitable crystal obtained from a CH_2Cl_2/hexane mixture, having the approximate dimensions 0.22 x 0.12 x 0.11 mm, was mounted in a non-specific orientation.

The structure was solved using standard Patterson techniques which gave the positional parameters for the Re atom. The remaining non-hydrogen atoms were located by the usual combination of least-squares refinement and difference Fourier synthesis.

Refinement of atomic parameters were carried out by full matrix least-squares techniques on F_0 minimizing the function

$$\Sigma w \left(|F_o| - |F_c| \right)^2$$

and the weighting factor w is given by

$$w = 4F_o^{\,2} \ / \ \sigma^2(F_o)^2$$

All hydrogen atoms were included at their idealized calculated distances, assuming C-H and B-H distances of 0.94Å.

In the final cycle, 190 parameters were refined using 2177 observations having $I > 2\sigma(I)$. The final agreement factors were:

$$R_1 = \Sigma \, | F_o | - | F_c | \ / \ \Sigma \, | F_o | \ = \ 0.0327$$

$$R_2 = [\, \Sigma w \, (| F_o | - | F_c | \,)^2 \ / \ \Sigma w \, F_o^{\,2} \,]^{1/2} \ = \ 0.0790$$

Table 3-4. Crystal Data and Details of Structure Refinement for HBPf$_3$Re(CO)$_3$ (5)

A. Crystal Data

$C_{18}H_{13}BF_9N_6O_3Re$ FW: 729.35

Crystal Dimensions: 0.22 x 0.12 x 0.11mm

Monoclinic space group P2$_1$/m (No. 11)

$a = 8.649(1)$, $b = 14.994(2)$, $c = 9.328(1)$ Å

$\beta = 100.839(8)^o$

$V = 1188.1(2)$ Å^3; $Z = 2$; $D_c = 2.039$ Mg/m^3

B. Data Collection and Refinement Conditions

Radiation (*l* [Å])	Mo K*a* (0.71073)
μ (mm^{-1})	5.218
F_{000}	696
Data collection *q* range (deg)	2.22 to 25.00
Index ranges	$-10 \le h \le 10, 0 \le k \le 17, 0 \le l \le 11$
Reflections collected	2177
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2177/0/190
Goodness-of-fit on F^2	1.044
Final R indices ($I>2\sigma(I)$)	$R_1 = 0.0327$, $wR_2 = 0.0790$
R indices (all data)	$R_1 = 0.0395$, $wR_2 = 0.0823$
Largest diff. peak and hole (e Å^{-3})	1.176 and -1.251

Table 3-5. Atomic Coordinates ($X10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2$ $X0^3$) for $HBPf_3Re(CO)_3$

Atom	*x*	*y*	*z*	U_{eq}
Re	4473(1)	2500	-1854(1)	42(1)
F(11)	1364(7)	-403(4)	-2129(6)	113(2)
F(12)	1673(10)	755(4)	-3250(6)	142(3)
F(13)	3568(8)	-74(6)	-2582(9)	157(3)
F(21)	8641(6)	1803(5)	-1921(7)	119(2)
F(22)	10465(6)	2500	-578(9)	91(2)
O(1)	5840(6)	1112(4)	-3669(6)	76(1)
O(2)	1605(9)	2500	-4314(9)	77(2)
N(11)	3499(5)	1501(3)	-507(5)	45(1)
N(12)	3617(5)	1666(3)	944(5)	45(1)
N(21)	6492(7)	2500	-7(8)	49(2)
N(22)	6196(8)	2500	1371(8)	49(2)
C(1)	5336(7)	1621(5)	-2952(7)	54(2)
C(2)	2646(11)	2500	-3380(11)	53(2)
C(11)	2338(9)	272(5)	-2178(9)	72(2)
C(12)	2710(7)	726(4)	-758(7)	52(1)
C(13)	2326(8)	399(4)	526(8)	59(2)
C(14)	2914(7)	1007(4)	1582(7)	56(2)
C(15)	2802(9)	995(5)	3165(7)	67(2)
C(21)	8921(11)	2500	-1069(13)	65(3)
C(22)	8058(9)	2500	151(11)	52(2)
C(23)	8748(10)	2500	1617(12)	62(3)
C(24)	7554(10)	2500	2388(12)	58(2)
C(25)	7610(13)	2500	3967(12)	83(3)
B	4462(11)	2500	1624(11)	46(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3-6. Bond Lengths (Å) for $HBPf_3Re(CO)_3$

Re–C(1)	1.905(7)	N(12)–B	1.525(7)
Re–C(2)	1.917(10)	N(21)–C(22)	1.335(10)
Re–N(21)	2.210(7)	N(21)–N(22)	1.358(10)
Re–N(11)	2.220(5)	N(22)–C(24)	1.364(11)
F(11)–C(11)	1.323(8)	N(22)–B	1.561(12)
F(12)–C(11)	1.280(10)	C(11)–C(12)	1.470(10)
F(13)–C(11)	1.301(9)	C(12)–C(13)	1.391(9)
F(21)–C(21)	1.308(8)	C(13)–C(14)	1.368(9)
F(22)–C(21)	1.328(11)	C(14)–C(15)	1.498(9)
O(1)–C(1)	1.154(8)	C(21)–C(22)	1.473(14)
O(2)–C(2)	1.129(11)	C(22)–C(23)	1.386(14)
N(11)–C(12)	1.345(8)	C(23)–C(24)	1.365(14)
N(11)–N(12)	1.361(7)	C(24)–C(25)	1.46(2)
N(12)–C(14)	1.355(8)		

Table 3-7. Bond Angles (deg) for HBPf$_3$Re(CO)$_3$

C(1)′–Re–C(1)	87.5(4)	N(21)–N(22)–B	120.0(7)
C(1)–Re–C(2)	87.3(3)	C(24)–N(22)–B	128.4(8)
C(1)′–Re–N(11)	178.1(2)	O(1)–C(1)–Re	177.1(6)
C(1)–Re–N(11)	93.8(2)	O(2)–C(2)–Re	177.6(9)
C(1)–Re–N(21)	95.0(2)	F(12)–C(11)–F(13)	105.7(9)
C(2)–Re–N(11)	94.2(2)	F(12)–C(11)–F(11)	105.3(7)
C(2)–Re–N(21)	176.9(3)	F(13)–C(11)–F(11)	105.4(7)
N(11)′–Re–N(11)	84.9(2)	F(12)–C(11)–C(12)	115.6(7)
N(21)–Re–N(11)	83.5(2)	F(13)–C(11)–C(12)	113.1(7)
C(12)–N(11)–N(12)	105.7(5)	F(11)–C(11)–C(12)	110.9(7)
C(12)–N(11)–Re	135.9(4)	N(11)–C(12)–C(13)	110.5(6)
N(12)–N(11)–Re	118.3(3)	N(11)–C(12)–C(11)	125.1(6)
C(14)–N(12)–N(11)	110.4(5)	C(13)–C(12)–C(11)	124.4(6)
C(14)–N(12)–B	129.4(6)	C(14)–C(13)–C(12)	105.6(5)
N(11)–N(12)–B	120.2(5)	N(12)–C(14)–C(13)	107.8(6)
C(22)–N(21)–N(22)	105.3(7)	N(12)–C(14)–C(15)	124.1(6)
C(22)–N(21)–Re	136.3(7)	C(13)–C(14)–C(15)	128.1(6)
N(22)–N(21)–Re	118.4(5)	F(21)′–C(21)–F(21)	106.0(10)
N(21)–N(22)–C(24)	111.6(7)	F(21)–C(21)–F(22)	105.6(6)
F(21)–C(21)–C(22)	114.0(6)	F(22)–C(21)–C(22)	110.9(9)
N(21)–C(22)–C(23)	110.4(9)	N(21)–C(22)–C(21)	124.5(9)
C(23)–C(22)–C(21)	125.2(8)	C(24)–C(23)–C(22)	107.0(8)
N(22)–C(24)–C(23)	105.7(9)	N(22)–C(24)–C(25)	124.1(9)
C(23)–C(24)–C(25)	130.2(9)	N(12)′–B–N(12)	110.2(7)
N(12)–B–N(22)	109.6(5)		

Primed atoms are related to unprimed ones via the symmetry transformation $x, {}^{1}/2-y, z$.

REFERENCES

1. Trofimenko, S. *J. Am. Chem. Soc.*, **1967**, *89*, 3170.

2. (a). Trofimenko, S. *Acc. Chem. Res.* **1971**, *4*, 17.
   (b). Trofimenko, S. *Chem. Rev.* **1972**, *72*, 497.
   (c). Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115.
   (d). Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.

3. (a). Calabrese, J. C.; Trofimenko, S.; Thompson, J. S. *J. Chem. Soc., Chem. Commun.* **1986**, 1122.
   (b). Rheingold, A.; White, C. B.; Trofimenko, S. *Inorg. Chem.* **1993**, *32*, 3471.
   (c). Cano, M.; Heras, J.; Trofimenko, S.; Monge, A.; Gutrerrez, E.; Jones, C.; McCleverty, J. *J. Chem. Soc., Dalton Trans.* **1990**, 3577.

4. (a). Ghosh, C. K.; Hoyano, J. K.; Krentz, R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1989**, *111*, 5480.
   (b). Krentz, R. PhD Thesis, University of Alberta, 1989.

5. (a). Angaroni, M.; Ardizzoia, G. A.; D'Alfonso, G.; La Monica, G.; Masciocchi, N.; Moret, M. *J. Chem. Soc. Dalton Trans.* 1990, 1895.
   (b). McCleverty, J. A.; Wolochowicz, I. *J. Organomet. Chem.* **1979**, 169, 289.

6. (a). Joachim, J. E.; Apostolidis, C.; Kanellakopulos, B.; Maier, R.; Marques, N.; Meyer, D.; Muller, J.; Pires de Matos, A.; Nuber, B.; Rebizant, J.; Ziegler, M. L. *J. Organomet. Chem.* **1993, 448**, 119.
   (b). Gan, L-B, PhD Thesis, University of Alberta, 1990.

7. Mesmeyanov, A. N.; Kolobova, N. E.; Makarov, Yu. V.; Anisimov, K. N. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1969**, *8*, 1826.

8. (a). Wright, J. B.; Dulin, W. E.; Markillie, J. H. *J. Med. Chem.* **1964**, *7*, 102.

   (b). Nishiwaki, T. *J. Chem. Soc. (B)* **1967**, 885.

   (c). Fields, R.; Tomlinson, J. P. *J. Fluor. Chem.* **1979**, *13*, 147.)

9. McCurdy, W. H. *Inorg. Chem.* **1975**, *14*, 2292.

10. Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

11. Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

12. (a). McCleverty, J. A.; Wlodarczyk, A. *Polyhedron* **1988**, *7*, 449.

    (b). Shiu, K-B.; Lee, L. Y. *J. Organomet. Chem.* **1988**, *348*, 357.

    (c). Shiu, K-B.; Curtis, M. D.; Huffman, J. C. *Organometallics* **1983**, *2*, 936.

    (d). Trofimenko, S. *Inorg. Chem.* **1970**, *9*, 1970.

13. Abel, E. W.; Hargreaves, G. B.; Wilkinson, G. *J. Chem. Soc.* **1958**, 3149.

14. Drago, R. S., *Physical Methods in Inorganic Chemistry*, Reinhold Publishing Corp.: NY, 1965, Chapter 11.

CHAPTER 4

SYNTHESIS AND REACTIVITY OF $[HBPf_3Mo(CO)_3]^-$

Section 1

INTRODUCTION

Pyrazolylborate chemistry has been extended to nearly all the transition metals, with the largest emphasis involving the Group six triad. However, most investigations have involved the use of the $HBPz_3$ and $HBPz^*_3$ ligands. Therefore, it was of interest to use the tris(3-trifluoromethyl-5-methylpyrazol-1-yl)borate ligand, and observe the effects of this electronically and sterically unique ligand.

It has been possible to synthesize $[Et_4N]^+ [HBPf_3Mo(CO)_3]^-$, and, as with its other pyrazolylborate analogues, it has provided an excellent starting point for the synthesis of new complexes. Also, the effect of the CF_3 groups in altering the electron donating power of the ligand can be established by comparing CO stretching frequencies with those of analogous compounds.

In solution there is no evidence for dissociation of the $[CpMo(CO)_3]_2$ dimer to radical monomer, although the radical species can be produced by irradiation. With the 3,5-disubstituted pyrazolylborate ligands, though, the size of the ligand can inhibit the formation of the dimer, and stabilize the seventeen-electron radical.[1] In this Chapter, we report the synthesis and properties of $HBPf_3Mo(CO)_3^{\bullet}$, as well as a comparison of its unusual thermal and air stability with those of the $HBPz_3$ and $HBPz^*_3$ analogues.

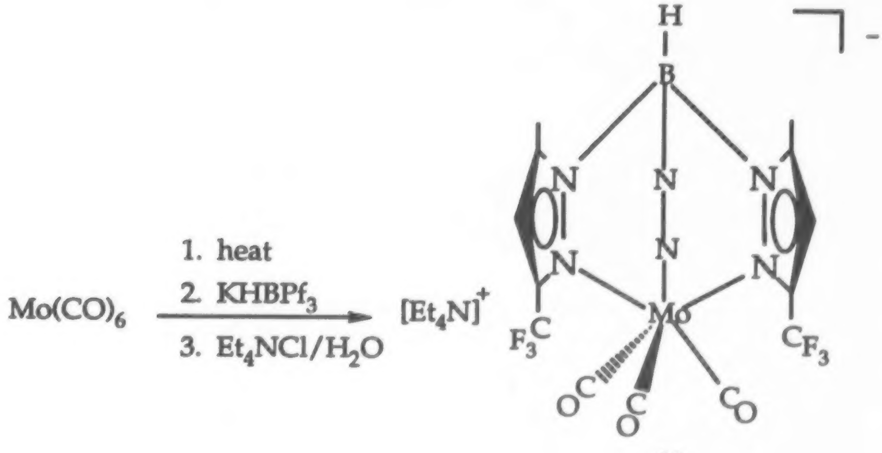
While complexes of the general formula $CpMoL_4$ and Cp^*MoL_4 (where L is a monodentate ligand) are common in cyclopentadienyl chemistry,[2] seven-coordinate pyrazolylborate compounds are less frequently encountered.[1a,3] This has mainly been attributed to the hybridization of the orbitals of the pyrazolylboratemolybdenum dicarbonyl fragment as compared to those of $CpMo(CO)_2$, and to the steric factors involved. Syntheses of $HBPz_3Mo(CO)_3H$[1c,4] and $HBPz^*_3Mo(CO)_3H$[3a] have been reported, and similar procedures have been used in this work to synthesize $HBPf_3Mo(CO)_3H$. This complex exhibits interesting spectroscopic behavior, and appears to be fluxional.

Transition metal nitrosyl chemistry has expanded greatly over the last 30 years and a recent book discusses the formation, characteristics and structures of many metal nitrosyl compounds.[5] McCleverty and coworkers[6] have synthesized numerous molybdenum and tungsten nitrosyl alkoxides of the form $HBPz^*_3Mo(NO)(X)(Y)$ (where X = halide, alkoxide; Y = alkoxide) and have noted the remarkable stability of these 16-electron complexes. This stability has been attributed to the size of the pyrazolylborate ligand preventing the approach of another ligand to relieve the metal of its unsaturation. The $HBPf_3$ ligand, having, presumably, a similar cone angle to that of the $HBPz^*_3$ ligand, should also provide stability to these complexes. X-ray structures of dialkoxy metal nitrosyl complexes have indicated short Mo-O bonds due to increased $p\pi \rightarrow d\pi$ interaction to compensate for the decrease in electron density around the unsaturated metal center.[6a,b] In this work, complexes of the form $HBPf_3Mo(NO)(Y)_2$ (Y = halide, alkoxide) have been synthesized and are discussed in Section 3.

Section 2

SYNTHESIS AND REACTIONS OF $[Et_4N]^+$ $[HBPf_3Mo(CO)_3]^-$

Much trispyrazolylborate chemistry has been carried out on the molybdenum metal center. However, no complexes using the $HBPf_3$ ligand have been synthesized. Use of the anions $[HBPz_3Mo(CO)_3]^-$ and $[HBPz^*{}_3Mo(CO)_3]^-$ has led to many new and interesting compounds. Consequently, a logical starting point was the synthesis of the analogous molybdenum tricarbonyl anion, $[Et_4N]^+$ $[HBPf_3Mo(CO)_3]^-$ **(10)**. When excess $KHBPf_3$ was added to the tris(acetonitrile)molybdenum tricarbonyl precursor, the resulting solution showed only two infrared carbonyl stretching bands (1911 and 1777 cm^{-1}). Addition of aqueous Et_4NCl (~0.8 M) resulted in the formation of yellow crystals in good yield (equation (4-1)).



10

(4-1)

NMR data are consistent with a species of C_{3v} symmetry as the ^1H NMR spectrum shows a singlet for the 4-H proton and for the 5-methyl group, as well as in the ^{19}F nmr at δ -59.50 ppm. NMR data for HPf, $HBPf_3$ and **10** are listed in Table 4-1. Coordination to the metal deshields the 5-Me and 4-H protons (Δδ ~ 0.4 ppm) and fluorines (Δδ ~ 6.5 ppm) of the pyrazolylborate ligand. Similar shifts in the ^{19}F NMR are found in all the molybdenum compounds presented in this Chapter.

Table 4-1. ^{1}H and ^{19}F NMR Data For Pf, $HBPf_3$, and $HBPf_3Mo(CO)_3^-$

	^{1}H		^{19}F
	δ (5-CH_3)	δ (4-H)	δ (3–CF_3)
Pf	2.35	6.36	-63.01
$HBPf_3^-$	2.16	6.17	-66.09
$HBPf_3Mo(CO)_3^-$ **(10)**	2.50	6.43	-59.50

All spectra run in acetone d_6, 200 MHz, ambient temperature.

Oxidation of $[Et_4N]^+ [HBPf_3Mo(CO)_3]^-$ (10)

The oxidation of **10** using $[Cp_2Fe]^+ [BF_4]^-$ in acetonitrile led to the formation of the red, crystalline 17-electron radical $HBPf_3Mo(CO)_3^{\cdot}$ **(11)** in good yield. Although a ^{1}H NMR spectrum containing three very broad peaks was obtained for the $HBPz^*_3Mo(CO)_3^{\cdot}$ analogue,[7] no signals at all could be observed in the ^{1}H NMR of **11**. However, infrared and mass spectra as well as an adequate elemental analysis were obtained. An effective magnetic moment of 2.24 BM, which is indicative of one unpaired electron, was measured using the Evans method.[8]

Infrared spectroscopy for this dark red complex indicated the presence of two CO stretching bands at 2031 and 1908 cm^{-1}, consistent with a complex having C_{3v} symmetry. A comparison of these infrared values to those of **10** indicates an increase of nearly 120 cm^{-1}. A comparison to the $HBPz^*_3$, $HBPz_3$ and Cp analogues is presented in Table 4-2.

Table 4-2. Comparison of Carbonyl Stretching Frequencies for Some 17-Electron Molybdenum Radicals

Complex	νCO (cm^{-1})[a]
$CpMo(CO)_3^{\cdot}$	1920 (m), 1845 (w)[b]
$HBPz_3Mo(CO)_3^{\cdot}$	2010 (s), 1885[c]
$HBPz^*_3Mo(CO)_3^{\cdot}$	1998 (s), 1864 (vs)[d]
$HBPf_3Mo(CO)_3^{\cdot}$ **(11)**	2025 (s), 1901 (s)

a. All spectra run in CH_2Cl_2 at room temperature.
b. In THF at 81K. (possibly THF-solvated)[9]
c. See reference 1a.
d. See reference 7.

From these data, it is possible to estimate the relative degree of back donation to the carbonyl ligands. As electrons begin to fill the π^* orbital of the carbonyl ligand, the C-O bond will weaken, and a lower infrared CO stretching frequency will result. In Table 4-2, the highest νCO value is obtained for the $HBPf_3$ radical. Therefore the $HBPf_3$ ligand is the poorest electron donor to the metal center. The presence of the CF_3 group on the pyrazole rings could account for the trend observed. With the high electronegativity of the fluorine, less electron density will be supplied by the ligand to the metal center, which in turn will have less electron density to donate to the carbonyls.

Complex **11** also exhibits remarkable stability. Crystals left at room temperature in an open container exhibited no decomposition over a six month period. Such high stability has also been noted for the $HBPz^{*}_3Mo(CO)_3^{\cdot}$ complex,[7] and contrasts the air-sensitive nature of the $HBPz_3Mo(CO)_3^{\cdot}$ complex, which showed decomposition even when stored under nitrogen.[1b] The added stability for the $HBPz^{*}_3$ complex has been attributed to the presence of the substituent in the 3-position of the pyrazole ring.[7] It was proposed that this substituent blocks the access to the metal center needed by an incoming ligand and prevents a facile pathway for decomposition. Since the $HBPf_3$ ligand possesses a substituent in the 3-position which is similar in size to the methyl group on the $HBPz^{*}_3$ ligand, it would seem reasonable to expect a similar result.

$HBPf_3Mo(CO)_3H$ (12)

The addition of concentrated HCl to an acetonitrile solution of **10** resulted in the formation, in good yield, of an analytically pure light-yellow microcrystalline precipitate **12** . Experimental results suggest that the hydrogen is more acidic rather than hydridic. For example, the need to use a strong acid to form this complex suggests that the anion, **10**, is a weak base. This differs from the $[CpMo(CO)_3]^-$ anion, which required only acetic acid to form the weak acid $CpMo(CO)_3H$.[10] Also, when **12** is dissolved in tetrahydrofuran or dimethylformamide, the infrared spectrum exhibits bands for **10** as well as **12**, while in nitromethane, only bands representing **10** are observed. Therefore, an acid-base equilibrium must exist between the hydride and the solvent. The acidity of hydrides of this type may account for

Curtis and Shiu's unsuccessful attempts to react HBPz$_3$Mo(CO)$_3$H with trityl.[3c]

Seven-coordinate complexes are of interest because they can provide useful information about mechanistic pathways for both associative and dissociative reactions.[11] Although seven-coordinate cyclopentadienylmolybdenum complexes are common, they are rarely formed when the sterically demanding pyrazolylborate ligand is present. Therefore, the synthesis of seven-coordinate pyrazolylborate compounds has presented interesting questions about possible geometry and fluxionality.

Through the use of ^{13}C NMR, it has been shown that the majority of cyclopentadienylmolybdenum compounds exhibit the four-legged piano stool (3:4 geometry) arrangement[2] (Figure 4-1(a)). With pyrazolylborate complexes, though, it was hoped that due to the size of the ligand it would be possible to observe complexes adopting either a 3:4 or 3:3:1 geometry (Figure 4-1(b)). Both possibilities are known to exist. Storr has crystallographically determined that [MeGaPz$_3$]Mo(CO)$_3$SnPh$_3$ adopts a 3:3:1 geometry,[12] while Curtis[3c] has shown that HBPz$_3$Mo(CO)$_3$Br adopts a 3:4 geometry.

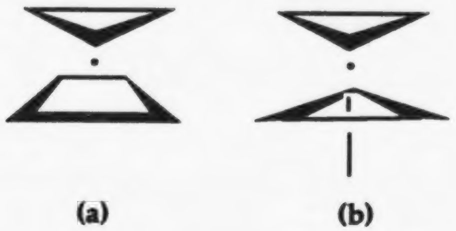


Figure 4-1. Possible Geometries for HBPf$_3$Mo(CO)$_3$H
(a). 3:4 (capped trigonal prism) (b). 3:3:1 (capped octahedron)

Interestingly, Faller[13] found that when a sample of CpW(CO)$_3$H (^{13}C enriched) was cooled below -70°C, two $^2J_{(H\text{-}W\text{-}^{13}CO)}$ coupling constants were observed consistent with a 3:4 conformation; when the sample was warmed above -70°C, only one value was observed. In order to explain the results above -70°C, he proposed that an intermediate of 3:3:1 geometry formed, placing all the carbonyls in the same environment on a time averaged basis (Figure 4-2).

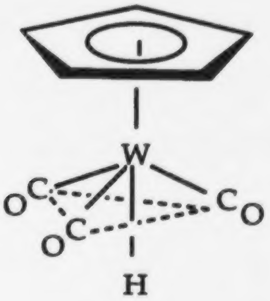


Figure 4-2. Faller's Proposed Intermediate to Explain Fluxionality

Many seven-coordinate complexes are known to be fluxional due to minimal energy differences between the idealized geometries (capped octahedron, pentagonal bipyramid, and capped trigonal prism).[11,14] Therefore, to observe fluxional behavior in HBPf$_3$Mo(CO)$_3$H (**12**) would not be surprising.

Similar to the experimental findings for the analogous HBPz$_3$ and HBPz*$_3$ molybdenum hydride complexes,[1c, 3a, 4] **12** also appears to be fluxional. Its infrared spectrum (Figure 4-3) exhibits three carbonyl stretching bands, suggesting a complex having C_s symmetry (3:4 conformation), and excluding a C_{3v} (3:3:1) structure. However, ^{1}H (Figure 4-4) and ^{19}F NMR spectra even at -80°C showed singlets for the 5-Me and 4-H protons on the

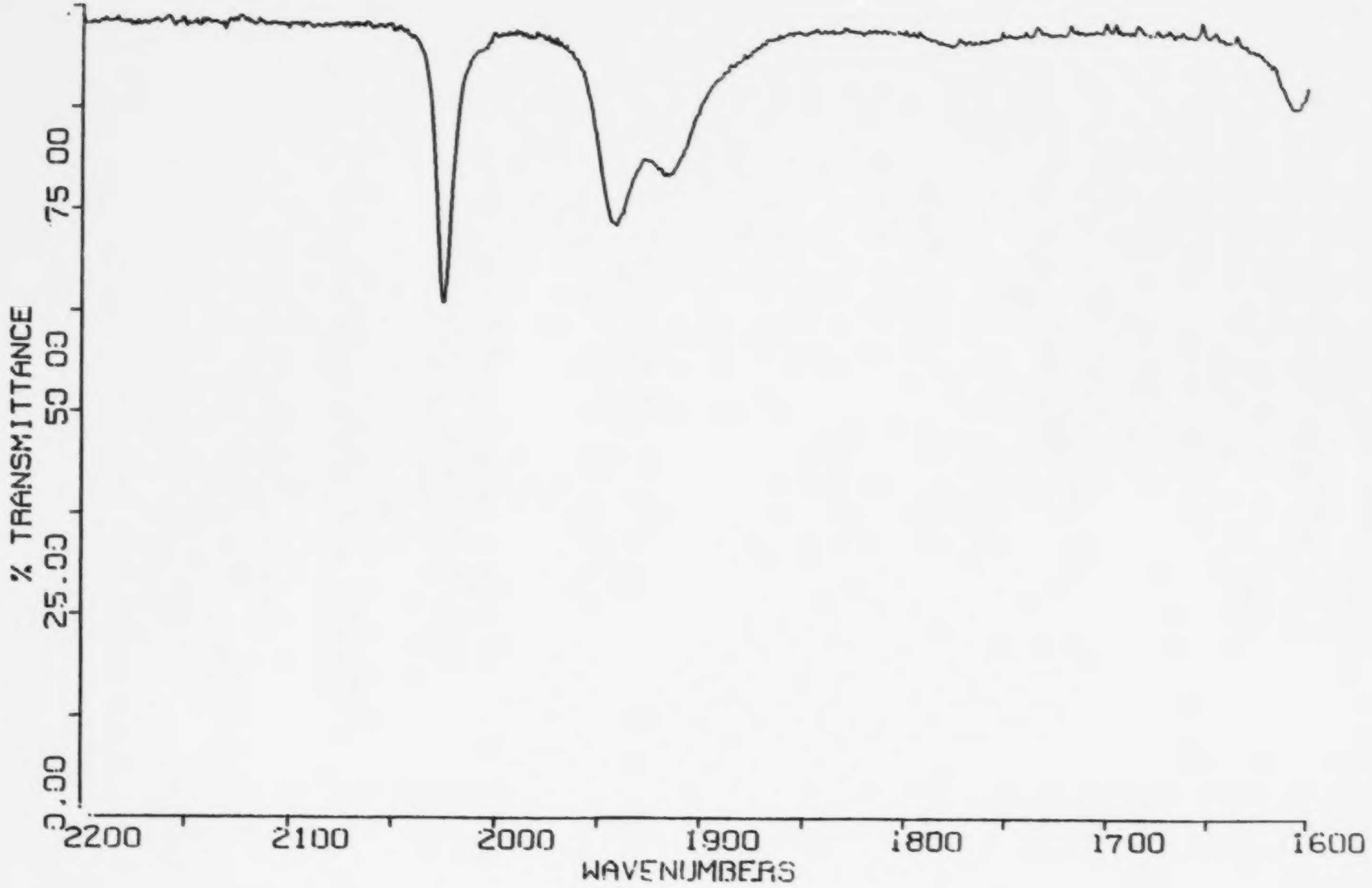


Figure 4-3. Infrared Spectrum of HBPf$_3$Mo(CO)$_3$H (12) (CH$_2$Cl$_2$)

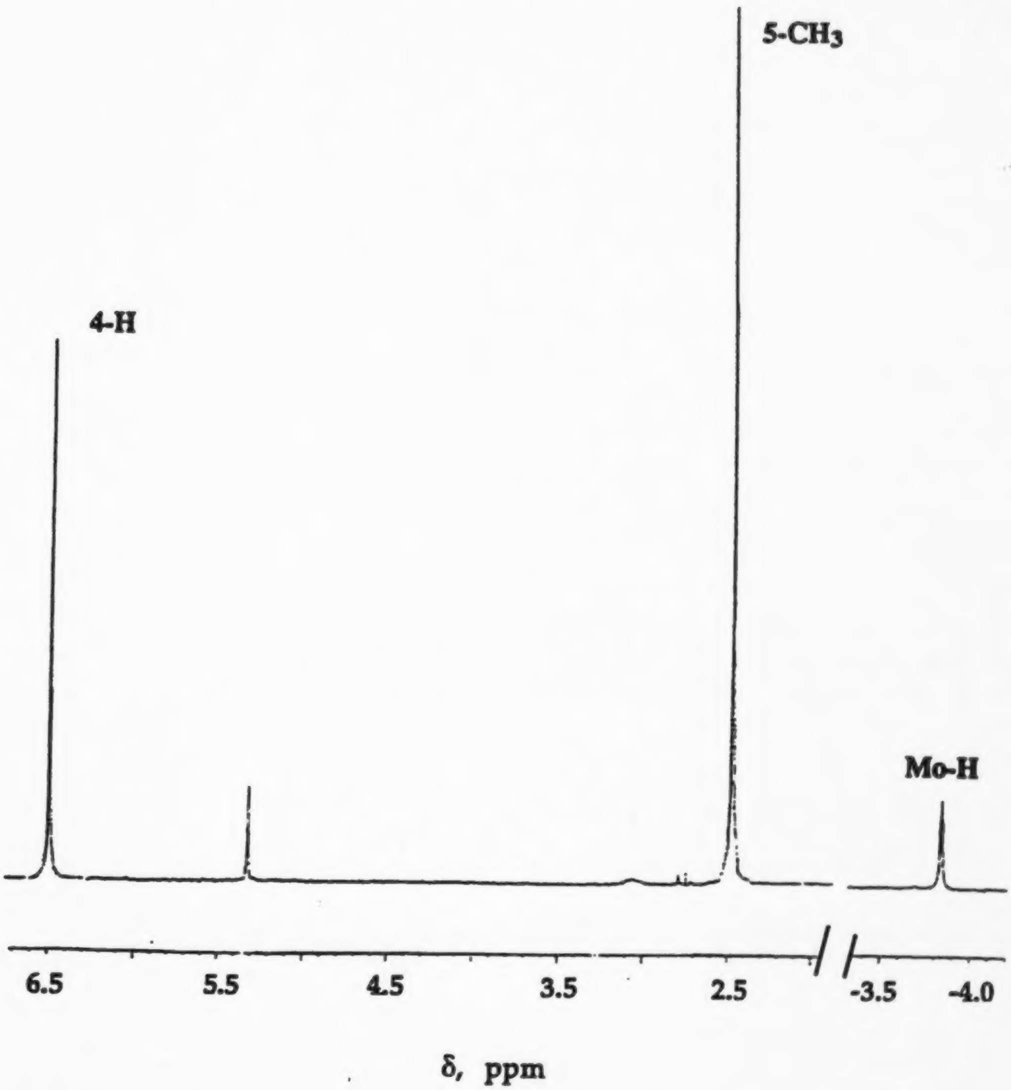


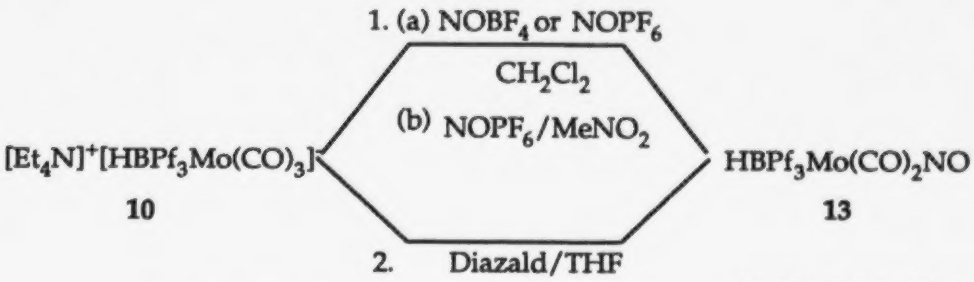
Figure 4-4. Room Temperature ^1H NMR of $HBPf_3Mo(CO)_3H$ (12)

pyrazole rings. This suggests a complex having a time averaged C_{3v} symmetry (3:3:1 geometry). For the $HBPz_3$ and $HBPz^*_3$ analogues, it has been suggested[3c] that the barrier for interconversion of the ligands in the basal plane of a 3:4 structure is less for pyrazolylborate complexes than the analogous Cp compounds, and that the 3:3:1 conformation is a viable intermediate for this fluxional process. This would also explain the results observed for **12**.

Curtis[3c] synthesized $HBPz_3Mo(CO)_3Br$ and also noted C_s symmetry in the infrared and C_{3v} symmetry in the NMR. In this case, a crystal structure conclusively showed the 3:4 geometry. Using the 3:4 structure as the ground state, EHMO methods were used to calculate the energies of possible isomers. Although the 3:3:1 isomer with a CO in the capping position was lower in energy than the isomer with a capping bromide, the time averaged singlet observed in the ^1H NMR spectrum can only be explained by the latter.

Ligand Substitution on $[HBPf_3Mo(CO)_3]^-$ (10)

Although numerous methods of replacing carbonyl ligands with nitrosyls exist,[15] two methods were used in this work in synthesizing $HBPf_3Mo(CO)_2NO$ **(13)**, and are summarized in Figure 4-5. Method 1(a) uses the nitrosonium salts $NOPF_6$ and $NOBF_4$, dissolved in solvent and added dropwise to the dissolved anion. Using acetonitrile or methylene chloride as solvents resulted in yields of approximately 45%. Refluxing **10** in tetrahydrofuran, acidifying the solution, and then adding Diazald (N-methyl-N-nitroso-p-toluenesulfonamide) gave comparable yields. The only advantage of using Diazald was the ease of handling the substance.



Yield: 1. (a) 45%
(b) 98%
2. 45%

Figure 4-5. Methods for Synthesizing $HBPf_3Mo(CO)_2NO$

As was also noted by Sweet[16] in synthesizing rhenium nitrosyls, use of the nitrosonium salts can be solvent dependent. For instance, by substituting nitromethane for acetonitrile, the yield of $[CpRe(CO)_2NO]^+$ increased from 80% to 91%. In this work, even greater improvement resulted: use of nitromethane increased the yield from 45% to greater than 90%.

The infrared spectrum of 13 exhibited three bands at 2041, 1963 (νCO) and 1714 (νNO) cm^{-1}. The ^1H NMR contained peaks in a 2:1 ratio for the 5-Me groups as well as the 4-H protons, while the ^{19}F NMR contained peaks in a 2:1 ratio for the CF_3 groups. Although the NO stretching frequency of 1714 cm^{-1} could indicate the presence of either a linear or bent nitrosyl, X-ray structures for similar complexes have indicated that a linear nitrosyl is present.[7]

Other Reactions

Curtis[3d] has synthesized η^2-acyl complexes by reacting $[HBPz_3Mo(CO)_3]^-$ with MeI or $[Me_3O]^+[BF_4]^-$. He postulated that their formation could be the result of the preference of the complex for coordination number six, due to the hybridization of the orbitals of the $HBPz_3Mo(CO)_2$ fragment. In this work, when $[Et_4N]^+ [HBPf_3Mo(CO)_3]^-$ was reacted with MeI or $[Me_3O]^+ [BF_4]^-$, no change was observed in the 2200 - 1600 cm^{-1} region of the infrared. This lack of reactivity could be a consequence of the size of the $HBPf_3$ ligand preventing the η^2-acyl from forming. It is also possible that the presence of the electron withdrawing CF_3 groups causes complex **10** to be a poorer nucleophile than with the $HBPz_3$ ligand. This would inhibit its interaction with the other reactants.

Section 3

THE CHEMISTRY OF $HBPF_3Mo(CO)_2NO$ (13)

The reactions of $LMo(CO)_2(NO)$ complexes (where L = $HBPz_3$ and $HBPz^*_3$) have been well investigated. McCleverty[7] demonstrated the ability of these compounds to form air stable, 16-electron molybdenum complexes of the form $HBPz^*_3Mo(X)(Y)(NO)$ (X = halide, alkoxide, Y = halide, alkoxide). Reaction of the dihalide complexes with alcohols resulted in mono- and disubstitution of the halogens. As a result, the chemistry of **13** was of interest in order to determine if similar results would be obtained with a less electron-donating pyrazolylborate ligand, and if steric differences between the ligands would affect the chemistry involved.

Halogenation

Synthesis of $HBPf_3Mo(NO)(Br)_2$ **(14)** was accomplished by adding a solution of Br_2 dropwise, at -30°C, to a methylene chloride solution of $HBPf_3Mo(NO)(CO)_2$ (equation (4-2)). The yellow solution slowly turned red-brown, and the infrared spectrum no longer contained bands for **13**. The red-brown product was obtained in good yield by recrystallization from methylene chloride and hexanes. The ^1H NMR spectrum showed two signals in 2:1 ratio for the 5-Me protons, as well as the 4-H protons, while the infrared spectrum exhibited one nitrosyl stretching band at 1658 cm^{-1}.

$$\underset{\textbf{13}}{HBPf_3Mo(CO)_2NO} + Br_2 \xrightarrow{-30^{o}C} \underset{\textbf{14}}{HBPf_3Mo(Br)_2NO} \qquad (4\text{-}2)$$

Ligand Substitution

Reaction of **14** with methanol or ethanol resulted in the formation of the bisalkoxy complexes $HBPf_3Mo(NO)(OR)_2$ (R = Me **(15)**, Et **(16)**), as violet and pink solids respectively. Although **14** could be stored in an open container for prolonged periods of time with no indication of decomposition, it was remarkably reactive. When a methylene chloride solution of **14** was layered with methanol or ethanol, a gradual color change occurred. When methanol was added, the solution slowly turned from the original orange-brown color to blue, purple and finally to violet over a period of several minutes. The infrared spectrum contained only one NO stretching band, while the ^{1}H NMR spectrum showed peaks in 2:1 ratio for the 5-Me and 4-H protons.

For the ethanol solution, the initially formed deep purple color exhibited infrared bands for starting material and product, and a small band mid-way between the two, presumably due to a monoethoxy intermediate. With continued stirring, the solution turned light pink. The ^{1}H NMR also contained peaks in a 2:1 ratio for the 5-Me and 4-H protons on the pyrazole ring. This differs from the chemistry of both the $HBPz_3$ and $HBPz^*_3$ molybdenum nitrosyl analogues. In both those instances, only monosubstitution occurred. Disubstitution resulted only upon addition of base, or after prolonged refluxing.

There are two possible explanations for the differing reactivities of $HBPz^*_3$, $HBPz_3$, and $HBPf_3Mo(X)_2NO$ complexes. The first deals with the size each ligand. For both the unsubstituted and dimethyl pyrazolylborate ligands, the diiodo complex could be synthesized. However, attempts to synthesize the analogous $HBPf_3$ complex were unsuccessful. This might imply that the $HBPf_3$ ligand is sterically more demanding. Therefore, it is possible that the dibromo complex **14** is also causing steric strain in the molecule, causing it to substitute the halides with the smaller alkoxide groups.

Although molybdenum prefers to form 18-electron complexes, both the dihalide and dialkoxy complexes contain 16 electrons. Consequently, the unsaturated metal center would prefer coordination with the alkoxy groups, as they are better π electron donating ligands. The effect of replacing a CO with an oxygen bound ligand was observed in the lowering of the CO bands in **5** when one CO was substituted with a THF molecule. Table 4-3 presents infrared data for the three 16-electron $HBPf_3Mo(X)_2NO$ complexes. Legzdins and Richter-Addo[17] indicated that the positions of νNO bands within similar complexes are indicative of the degree of electron donation from the metal to the nitrosyl π* orbital. Consequently, the complex containing the most electron-donating ligand (OEt) has the lowest νNO band, while the dihalide complex has the least electron donation to the antibonding orbital.

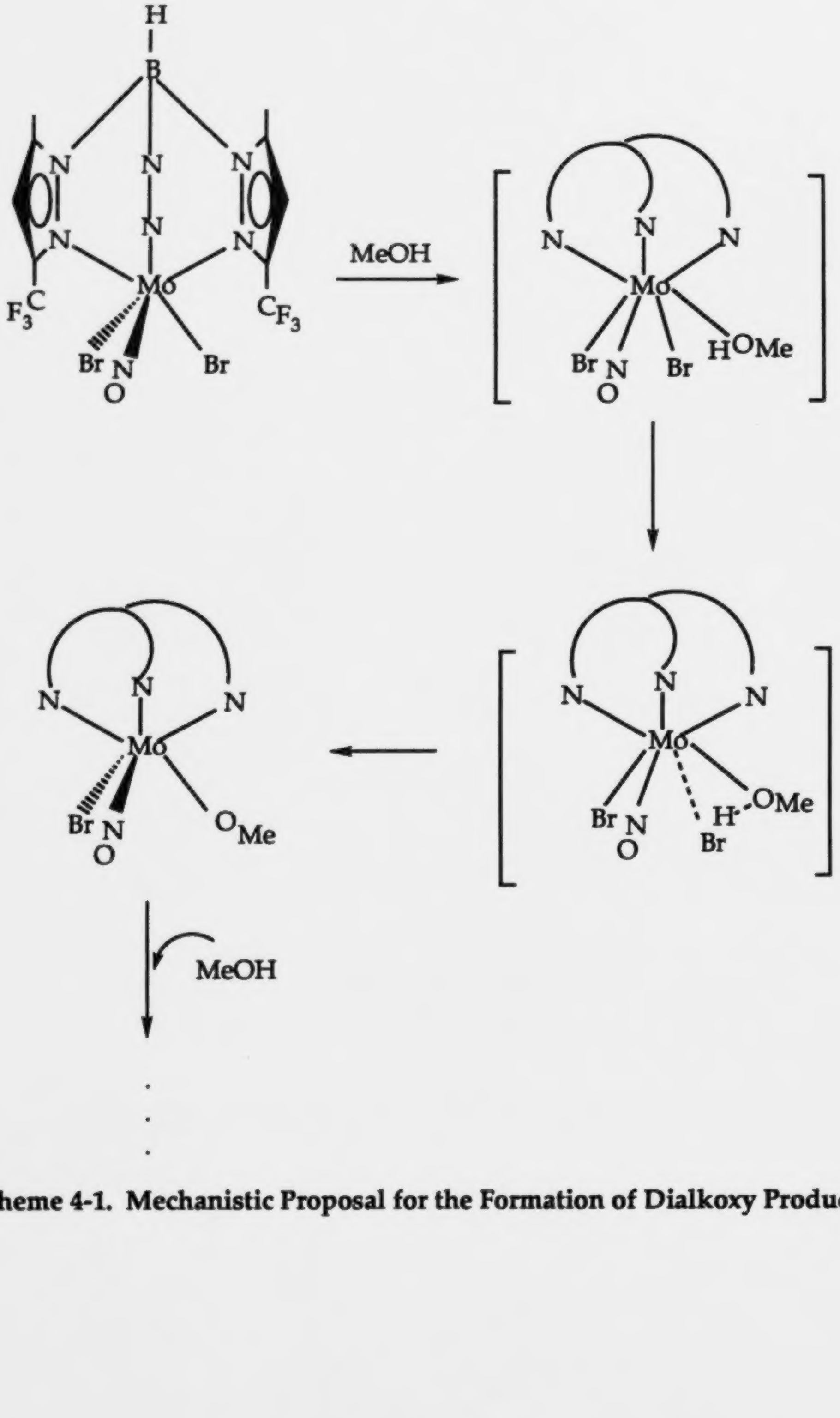
Table 4-3. Stretching Frequencies of Molybdenum Nitrosyl Complexes

Complex	νNO (cm^{-1})
$HBPf_3Mo(Br)_2NO$ (14)	1758[a]
$HBPf_3Mo(OMe)_2NO$ (15)	1685[b]
$HBPf_3Mo(OEt)_2NO$ (16)	1676[a]

a. Recorded in CH_2Cl_2 solvent.
b. Recorded in $CHCl_3$ solvent.

Therefore, the alkoxy groups are able to provide extra electron donation to the unsaturated metal center.

A schematic reaction pathway associated with the formation of the dialkoxy complexes is illustrated in Scheme 4-1. The lone pairs on the oxygen can attach to the metal center, creating a seven-coordinate, 18-electron, intermediate. The acidic hydrogen on methanol will be in close proximity to the bromide ligand, and could result in the loss of HBr. This monosubstituted product is presumably the one observed in the infrared spectrum of $HBPf_3Mo(NO)(OEt)_2$ as a band observed mid-way between the starting material and the product. Repeating this scheme would result in the formation of the disubstituted product.


H
B
N
N
N
N
N
N
Mo
F3C
CF3
Br
N
O
Br
MeOH
N
N
N
Mo
Br
N
O
Br
HOMe
N
N
N
Mo
Br
N
O
H
Br
OMe
N
N
N
Mo
Br
N
O
OMe
MeOH

Scheme 4-1. Mechanistic Proposal for the Formation of Dialkoxy Products

Section 4

EXPERIMENTAL

All manipulations were carried out under an inert atmosphere using standard Schlenk techniques. Other solvents were used as received from suppliers. Deaeration of solvent was accomplished by bubbling argon through the solvent using a gas dispersion tube of porosity A or B for 20 minutes prior to use.

Preparation of $[Et_4N]^+ [HBPf_3Mo(CO)_3]^-$ (10)

A sample of $Mo(CO)_6$ (581 mg, 2.23 mmol) dissolved in 120 mL acetonitrile was refluxed for 23h. $KHBPf_3$ (1.850 g, 3.72 mmol) was added, and the solution refluxed for 4h. Once the solution was concentrated to approximately 2/3 the original volume, Et_4NCl (6.104 g, 36.9 mmol) in 55 mL deaerated water was introduced. This resulted in the formation of a yellow oil which, after storing at 5 ^oC overnight, afforded yellow crystals. (1.055 g, 61%).

Characterization: IR (MeCN): 1913 (vs), 1780 (vs) vCO (CH_2Cl_2): 1980 (vs), 1777(vs). MS, -ve FAB (m/e, rel. int.): M^- (639, 28), $M\text{-}CO^-$ (611, 2), $M\text{-}3CO^-$ (555, 1), $HBPf_3^-$ (459, 60), $Mo(CO)_3^-$ (180, 5). ^1H NMR (acetone d_6): δ 1.40 (t of t , 12 H), 2.50 (s, 9H), 3.50 (q, 8H), 6.43 (s, 3H). ^{19}F NMR (acetone d6): δ -59.50 (s, 9F). Anal. Calcd for $C_{26}H_{33}F_9N_7O_3BMo$: C 40.59, H 4.32, N 12.74. Found: C 40.71, H 4.37, N 12.66.

Synthesis of $HBPf_3Mo(CO)_3^{\bullet}$ (11)

Ferrocenium tetrafluoroborate (24.0 mg, 88.4 mmol) in 10 mL CH_2Cl_2 was added to a solution of **10** (68 mg, 88.4 mmol) in 20 mL CH_2Cl_2. The solution slowly turned red, and red crystals could be seen on standing. These were filtered and dried in vacuo (30 mg, 52%). μ_{eff} = 2.24 BM.

Characterization: IR(Hexanes): 2031 (s), 1908 (m, vbr) νCO. MS, +ve FAB (m/e, rel. int.): M^+ (641, 2), $M\text{-}CO^+$ (613, 3), $M\text{-}2CO^+$ (587, 10), $M\text{-}3CO^+$ (557, 6). Anal. Calcd for $C_{18}H_{13}N_6F_9BMoO_3$: C 33.83, H 2.05, N 13.15. Found: C 34.07, H 1.93, N 12.95. ^1H NMR and ^{19}F NMR were not obtained.

Synthesis of $HBPf_3Mo(CO)_3H$ (12)

Concentrated HCl (0.170 mL) was added to **10** (108 mg, 0.168 mmol) in 5 mL MeCN. A light-yellow precipitate immediately formed. This was isolated and dried in vacuo. (215 mg, 50%)

Characterization: IR(THF): 2041 (vs), 1941 (vs), 1915 (vs) (KBr): 2027 (m), 1940 (m), 1928 (m) νCO. MS, 180 °C/16 eV (m/e, rel. int.): M^+ (640, 43), $M\text{-}CO^+$ (612, 60), $M\text{-}2CO^+$ (584, 12), $M\text{-}3CO^+$ (556, 100). ^1H NMR (CD_2Cl_2): δ -3.84 (s, 1H), 2.47 (s, 9H), 6.50 (s, 3H). ^{19}F NMR ($CDCl_3$): -59.08 (s, 9F). Anal. Calcd for $C_{18}H_{14}N_6F_9BMoO_3$: C 33.78, H 2.20, N 13.13. Found: C 33.80, H 2.01, N 12.85.

Synthesis of $HBPf_3Mo(CO)_2(NO)$ (13)

(a). A sample of 10 (502 mg, 0.652 mmol) in 120 mL nitromethane, was cooled to -30 °C. $NOPF_6$ (177 mg, 1.01 mmol) in 20 mL nitromethane was added dropwise until the infrared spectrum indicated complete conversion to product. The solution was stored at -20 °C for 2 days, by which time a yellow precipitate had formed. The precipitate was separated and dried under vacuum. The remaining solvent was stripped on the rotary evaporator, leaving a yellow-orange precipitate. This was recrystallized with a CH_2Cl_2-MeOH (1:1) mixture yielding a yellow precipitate (409 mg, 98%).

Characterization: IR (Hexanes): 2041 (w, νCO), 1963 (w, νCO), 1714 (w, νNO). MS, 250 °C/70 eV (m/e, rel. int.): M^+ (643, 2), $M\text{-}CO^+$ (615, 10), $M\text{-}NO^+$ (613, 8), $M\text{-}2CO^+$ (587, 55), $M\text{-}NO\text{-}2CO^+$ (557, 9). ^1H NMR ($CDCl_3$): δ 2.48 (s, 3H), 2.51 (s, 6H), 6.42 (s, 1H), 6.48 (s, 2H). ^{19}F NMR ($CDCl_3$): δ -59.97 (s, 6F), -58.74 (s, 3F). Anal. Calcd for $C_{17}H_{13}N_7F_9MoO_3B$: C 31.85, H 2.04, N 15.29. Found: C 31.78, H 2.06, N 14.60.

(b). A sample of $Mo(CO)_6$ (1.14g, 4.34 mmol) and $KHBPf_3$ (3.2207g, 6.47 mmol) were added to 200 mL dry MeCN and refluxed overnight. Acetic acid (8 mL) was added and the solution was stirred for 3 hours. Then, Diazald (0.92g, 4.34 mmol) was added and the solution stirred overnight. The solvent was removed under vacuum and the black residue dissolved in dry methanol. After several days, a yellow precipitate formed. This was filtered off and dried under vacuum. (1.25 g, 45%)

Synthesis of $HBPf_3Mo(Br)_2NO$ (14)

Bromine (65.2 mg, 0.021 mL, 0.408 mmol), in 10 mL CH_2Cl_2, was added dropwise to a -30 °C solution of 13 (261 mg, 0.408 mmol) in 50 mL CH_2Cl_2. After the addition was complete, the solution was allowed to warm slowly to room temperature, and was stirred overnight. The solvent was concentrated to half its original volume and layered with hexanes, yielding an orange-brown precipitate (294 mg, 97%).

Characterization: IR(CH_2Cl_2): 1758 (vs, νNO). MS 200 °C/70 eV (m/e, rel. int.): M+ (745, 24), M-NO+ (715, 32), M-Br+ (665, 8), M-NO-Br+ (635, 11). ^{1}H NMR (CD_2Cl_2): δ 2.48 (s, 6H), 2.61 (s, 3H), 6.62 (s, 2H), 6.66 (s, 1H). ^{19}F NMR (CD_2Cl_2): δ -59.73 (s, 6F), -55.63 (s, 3F). Anal. Calcd for $C_{15}H_{13}N_7F_9BMoBr_2O$: C 24.19, H 1.76, N 13.16, Br 21.45. Found: C 24.34, H 1.76, N 12.59, Br 21.62.

Synthesis of $HBPf_3Mo(OMe)_2NO$ (15)

A sample of 14 (35.1 mg, 40.3 mmol) in 10 mL CH_2Cl_2 was layered with 10 mL MeOH. The color progressed from red-orange to dark green to blue to dark purple. The solution was slightly concentrated, and stored at -30 °C, where purple crystals appeared. These were filtered and dried under vacuum (21.1 mg, 81%).

Characterization: IR($CHCl_3$): 1685 (s) νNO. MS, +ve FAB (m/e, rel. int.): M^+ (649, 7), M-OMe^+ (618, 19), M-2OMe^+ (587, 2). ^{1}H NMR ($CDCl_3$): δ 2.46 (s, 9H), 5.04 (s, 6H), 6.41 (s, 1H), 6.49 (s, 2H). ^{19}F NMR ($CDCl_3$): δ -60.18

(s, 6F), -60.65 (s, 3F). Crystallization incorporated 2.5 mole CH_2Cl_2. Anal. Calcd for $C_{17}H_{19}N_7F_9BMoO_3 \cdot 2.5CH_2Cl_2$: C 30.66 H 2.91, N 14.58. Found: C 30.54, H 2.67, N 14.29.

Synthesis of $HBPf_3Mo(OEt)_2NO$ (16)

To **14** (37.5 mg, 50.4 µmol) in 10 mL CH_2Cl_2 was added 1.5 mL EtOH (99.9%) and the solution allowed to stir. The solution color changed from orange/brown to deep purple in minutes. The solution was stirred overnight, at which time the color had become a paler purple. An infrared spectrum exhibited bands at 1716 (monosubstituted species) and 1675 (**16**) cm^{-1} in a 1:1 ratio. Continued stirring led to the formation of a pink solution. The solvent was removed under vacuum, leaving a pink solid. (20.4 mg, 60%)

Characterization: IR (CH_2Cl_2): 1676 (m), νNO. MS 200 °C/70 eV (m/e, rel. int.): M^+ (677, 28), $M\text{-}NO^+$ (647, 22), $M\text{-}OEt^+$ (632, 2). ^1H NMR (CD_2Cl_2): δ 1.28 (t, 3H, $J_{H\text{-}H}$ = 7.2 Hz), 2.47 (s, 6H), 2.51 (s, 3H), 5.34 (q, 2H), 6.45 (s, 1H), 6.53 (s, 2H). ^{19}F NMR (CD_2Cl_2); δ -59.61 (s, 3F), -60.62 (s, 6F). Anal. Calcd for $C_{19}H_{23}N_7F_9BMOO_3$: C 33.79, H 3.41, N 14.52. Found: C 33.71, H 3.56, N 12.80.

REFERENCES

1. (a). Curtis, D. M.; Shiu, K-B.; Butler, W. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1986,** *108,* 3335.

   (b). Shiu, K-B.; Curtis, D. M.; Huffman, J. C. *Organometallics,* **1983,** 2, 936.

2. Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds., *Comprehensive Organometallic Chemistry,* Vol. 3, Pergamon: Oxford, 1982, p. 1176-1204.

3. (a). Trofimenko, S. *J. Am. Chem. Soc.* **1969,** *91,* 588.

   (b). Greaves, W. W.; Angelici, R. J. *J. Organomet. Chem.* **1980,** *191,* 49.

   (c). Curtis, M. D.; Shiu, K-B. *Inorg. Chem.* **1985,** *24,* 1213.

   (d). Curtis, M. D.; Shiu, K-B.; Butler, W. M. *J. Am. Chem. Soc.* **1986,** *108,* 1550.

   (e). Curtis, M. D.; Shiu, K-B.; Butler, W. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1986,** *108,* 3335.

   (f). Philipp, C. C.; White, P. S.; Templeton, J. L. *Inorg. Chem.* **1992,** *31,* 3825.

   (g). Onyiriuka, E. C.; Storr, A. *Can. J. Chem.* **1987,** *65,* 2464.

   (h). Liu, Y-Y.; Mar, A.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1988,** *66,* 1997.

   (i). Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1988,** *66,* 2194.

4. Caffyn, A. J. M.; Feng, S. G.; Dierdorf, A.; Gamble, A. S.; Eldredge, P. A.; Vossen, M. R.; White, P. S.; Templeton, J. L. *Organometallics* **1991,** *10,* 2842.

5. Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls,* Oxford University Press: New York, 1992.

6. (a). McCleverty, J. A.; Seddon, D.; Bailey, N. A.; Wlaker, N. A. *J. Chem. Soc. Dalton Trans.,* **1976,** 898.

(b). McCleverty, J. A.; Rae, A. E.; Wolochowicz, I.; Bailey, N. A.; Smity, J. M. A. *J. Chem. Soc. Dalton Trans.* **1982**, 951.

(c). McCleverty, J. A.; Wlodarczyk, A. *Polyhedron* **1988**, *7*, 449.

(d). Cano, M.; Heras, J. V.; Trofimenko, S.; Monge, A.; Gutierrez, E.; Jones, C. J.; McCleverty, J. A. *J. Chem. Soc. Dalton Trans.* **1990**, 3577.

(e). McCleverty, J. A.; Rae, E. A.; Wolochowicz, I.; Bailey, N. A.; Smith, J. M. A. *J. Chem. Soc., Dalton Trans.* **1982**, 429.

7. Shiu, K-B.; Lee, L-Y. J. *Organomet. Chem.* **1988**, *348*, 357.

8. Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

9. Allen, D. M.; Cox, A.; Kemp, T. J.; Sultana, Q. *Inorg. Chim. Acta* **1977**, *21*, 191.

10. Fischer, E. O. *Inorg. Synthesis* **1963**, *7*, 136.

11. Hoffmann, R.; Beier, B. F.; Muetterties, E. L.; Rossi, A. R. *Inorg. Chem.* **1977**, *16*, 511.

12. Onyiriuka, E. C.; Rettig, S. J.; Storr, A. *Can. J. Chem.* **1986**, *64*, 321.

13. Faller, J. W.; Anderson, A. S.; Chen, C-C. *Chem. Commun* **1969**, 719.

14. Thompson, H. B.; Bartell, L. S. *Inorg. Chem.* **1968**, 7, 488.

15. Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*, Oxford University Press: New York, 1992, p. 1-15.

16. Sweet, J. PhD Thesis, University of Alberta, 1981.

17. Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*, Oxford University Press: New York, 1992, p. 61-62.

CHAPTER 5

SUMMARY AND CONCLUSIONS

Ligands containing the 3-trifluoromethyl-5-methylpyrazolyl group (HPf) have been studied. Reaction of HPf with diiodomethane afforded the new bis(3-trifluoromethyl-5-methylpyrazol-1-yl)methane ligand (CH_2Pf_2) (**1**), which reacted with $[Re(CO)_4(\mu\text{-}Br)]_2$ to produce *fac*-$CH_2Pf_2Re(CO)_3Br$ (**2**). Reaction of **2** with PMe_3 or PMe_2Ph has resulted in the substitution of the ligand **1** by two phosphine groups, forming the *fac*-$Re(CO)_3(PR_2R')_2Br$ isomer. This displacement of the chelated ligand is thought to be a result of weaker Re-N bonds, in relation to the Re-CO bonds, in **2**. Weaker Re-N bonds could be due to the presence of the electron withdrawing CF_3 groups on the pyrazole ring.

As a continuation of this project, it would be useful to synthesize the $H_2CPz^*_2$ (bis(3,5-dimethylpyrazol-1-yl)methane) and H_2CPz_2 (bispyrazolylmethane) analogues of **2**, and react them with various phosphine groups in order to determine the role the electron donating (withdrawing) substituents play in the chemistry observed.

The chemistry of the $HBPf_3$ ligand, synthesized by Graham and Krentz,[1] has now been expanded to rhenium and molybdenum metal centers. The rhenium complex $HBPf_3Re(CO)_3$ (**5**) was prepared, and exhibited no reaction when stirred with bromine. This is in contrast with the chemistry observed for the $HBPz^*_3$ analogue, where the 4-H of the pyrazole ring, was substituted by a bromide.[2] This could be a result of the size of the substituents on the pyrazole ring, or due to the partial charges on the 4-C in 3-trifluoromethyl-5-methylpyrazole, as compared to the dimethyl and unsubstituted pyrazole analogues. The synthetic application arising from substitution of the 4-hydrogen (in complexes where it occurs) appears to have received little attention. It might provide a convenient avenue to otherwise inaccessable funtionally substituted pyrazolylborates.

Photolysis of **5** in THF has resulted in the substitution on one CO to form $HBPf_3Re(CO)_2THF$ (**6**). Reaction of **6** with Br_2 and CCl_4 resulted in the formation of the air-stable seventeen-electron radicals $HBPf_3Re(CO)_2X^{\cdot}$ (X = Br, Cl). The measurement of their effective magnetic moments indicated a single unpaired electron.

In the case of molybdenum, $HBPf_3$ was used to synthesize $[Et_4N]^+$ $[HBPf_3Mo(CO)_3]^-$ (**10**). The oxidation of **10** with ferrocenium ion resulted in the formation of the seventeen-electron radical $HBPf_3Mo(CO)_3^{\cdot}$ (**11**), which exhibited unusual air stability. This stability has been attributed in a related case to the large size of the pyrazolylborate ligand, which protects the metal center from the approach of another ligand.[3]

The addition of concentrated HCl to **10** formed the seven-coordinate complex $HBPf_3Mo(CO)_3H$ (**12**). Although its infrared spectrum exhibited three carbonyl stretching bands, consistent with C_s symmetry (3:4 coordination geometry), its NMR spectrum indicated the equivalence of the three pyrazoles. As in the earlier work of Curtis[4] on $HBPz_3Mo(CO)_3Br$, it would appear that **12** is fluxional, with a 3:3:1 geometry as a likely transition state or intermediate, in an averaging process. This would explain the appearance of a singlet for the three pyrazoles.

Reaction of **10** with nitrosonium salts resulted in the formation of $HBPf_3Mo(CO)_2NO$ (**13**). A marked increase in the yield of **13** occurred if nitromethane was used as the solvent, instead of acetonitrile or dichloromethane. It was also possible to synthesize **13** by acidifying a tetrahydrofuran solution of **10** and adding Diazald. The reaction of **13** with bromine resulted in the substitution of the carbonyls with bromide, forming $HBPf_3Mo(Br)_2NO$ (**14**). Although **14** is a sixteen-electron complex, it exhibits air and thermal stability. It is, however, very reactive. Layering a methylene chloride solution of **14** with methanol or ethanol results in the substitution of the bromides by two alkoxides. This differs from the reaction of the analogous $HBPz_3$ and $HBPz^*_3$ complexes, where only monosubstitution occurs.[5] This may be due to the metal center attempting to compensate for its unsaturated state as the alkoxide ligands are better π electron-donating ligands than the bromides.

It would be interesting to react **14** with various ligands, such as t-butyl alcohol, in an attempt to substitute only one bromide ligand, forming a chiral complex. It might then be possible to substitute the remaining bromide with an alkyl group. It would also be interesting to investigate the possibility of synthesizing a dialkyl product. Legzdins[6] has found that $CpMo(NO)R_2$ complexes ($R = CH_2SiMe_3$, CH_2CMe_3, CH_2CMe_2Ph, Ph, p- or o-tolyl) can be formed using R_2Mg-dioxane. However, the final products exhibit some air or thermal instability. He has shown[7] that by increasing the size of the substituents on the Cp ring, greater stability can be achieved. Therefore, the larger trispyrazolylborate ligand should provide added stability to complexes with smaller R groups.

REFERENCES

1. (a). Ghosh, C. K.; Hoyano, J. K.; Krentz, R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1989**, *111*,5840.

   (b). Krentz, R. PhD. Thesis, University of Alberta, 1989.

2. McCleverty, J. A.; Wolochowicz, I. *J. Organometallic Chemistry* **1979**, *169*, 289.

3. (a). Shiu, K-B.; Lee, L-Y. *J. Organomet. Chem.* **1988**, *348*, 357.

   (b). Curtis, D. M.; Shiu, K-B.; Butler, w. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3335.

   (c). Shiu, K-B.; Curtis, D. M.; Huffman, J. C. *Organometallics*, **1983**, 2, 936.

4. Curtis, M. D.; Shiu, K-B. *Inorg. Chem.* **1985**, *24*, 1213.

5. (a). McCleverty, J. A.; Seddon, D.; Bailey, N. A.; Walker, N. A. *J. Chem. Soc., Dalton Trans.* **1976**, 898.

   (b). McCleverty, J. A.; Rae, A. E.; Wolochowicz, I.; Bailey, N. A.; Smity, J. M. A. *J. Chem. Soc., Dalton Trans.* **1982**, 951.

   (c). McCleverty, J. A.; Wlodarczyk, A. *Polyhedron* **1988**, *7*, 449.

   (d). Cano, M.; Heras, J. V; Trofimenko, S.; Monge, A.; Gutierrez, E.; Jones, C. J.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1990**, 3577.

6. (a). Legzdins, P.; Rettig, S. J.; Sanchez, L. *Organometallics* **1988**, *7*, 2394.

   (b). Legzdins, P.; Rettig, S. J.; Sanchez, L. *J. Am. Chem. Soc.* **1985**, *107*, 1411.

   (c). Dryden, N. H.; Legzdins, P.; Rettig, S. J.; Veltheer, J. E. *Organometallics*, **1992**, *11*, 2583.

   (d). Legzdins, P.; Veltheer, J. E. *Acc. Chem. Res.* **1993**, *26*, 41.

7. Legzdins, P.; Reina, R.; Shaw, M. J.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1993,** *12,* 1029.